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CONDUCTED BY

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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

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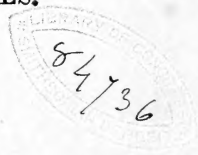
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Meditationis est perscrutari occulta; contemplationis est admirari  
perspicua . . . . . Admiratio generat quæstionem, quæstio investigationem,  
investigatio inventionem."—*Hugo de S. Victore.*

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—"Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condat,  
Quid toties diros cogat flagrare cometas;  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu."

*J. B. Pinelli ad Mazonium.*

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[FOURTH SERIES.]

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JANUARY 1875.

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I. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE\*.

§ 1. **T**HE interesting paper read to the Physical Society of London by Dr. J. Rae, the arctic explorer, on the comparative saltness of freshly formed and older ice-floes†, induced me to examine some of the physical properties of brine and some other of the aqueous solutions of the salts of the sea. This examination has extended itself to some other salts; for before attacking the problem of the freezing of sea-water, the composition of which may be little less complex than that of the earth itself, it seemed advisable to enrich our knowledge of the properties of the solutions of some of its more abundant constituents in the separate form. Some of the experimental results unexpectedly opened so wide and fascinating a field of inquiry, that I have been compelled to make some sort of survey of it; and though the results there gathered are of sufficient interest to be considered by themselves as physical facts, they will assuredly also be concerned in the establishment of a sufficient theory of thalattology.

*Chloride of Sodium.*

§ 2. Being fortunately in possession of a large quantity of extremely pure rock-salt in fine crystals, I satisfied myself by the spectroscope of the absence of potassium and lithium. By the usual tests, magnesium and sulphuric acid were also shown to be absent. A determination of the chlorine agreed so closely with the theoretical quantity that not more than 0.2 per cent.

\* Read before the Physical Society, November 7, 1874. Communicated by the Society.

† Proc. Phys. Soc. May 9, 1874. Phil. Mag. July 1874, p. 56.

Phil. Mag. S. 4. Vol. 49. No. 322. Jan. 1875.

of any metal having an atomic weight differing by more than 5 from that of sodium could be present, supposing it to be a chloride. On converting the chloride into a sulphate an equally accordant result was got. This convinced me that I had a perfectly pure substance.

§ 3. *Preparation of the Brine.*—The clearest lumps of the rock-salt were washed in common and then in distilled water. With these a large beaker was filled. Distilled water was poured on so as to fill the beaker about two thirds. If part of the salt is thus always above the surface of the brine, the latter appears to be saturated in twenty-four hours. After forty-eight hours the brine was poured into another beaker and allowed to stand until crystals began to be formed. It was then transferred to a stoppered bottle and was ready for use. Although Regnault and others have shown that for temperatures above  $0^{\circ}$  C. the solubility of chloride of sodium in water is constant, yet the precaution was taken of suspending a muslin bag containing some crystals of salt from a string passing through the cork of the bottle so that the crystals touched the surface of the brine. By this means the perfect saturation of the brine was assured. At  $18^{\circ}$  C. this solution contained 26.2724 per cent. of salt. The solution was weighed in a long-necked flask, and was evaporated to dryness and heated to about  $300^{\circ}$  C.

The following numbers show the results obtained by some other experimenters:—

			per cent.	spec. grav.
Kopp	Sat. at $25^{\circ}$ C.	contains	26.32	
Kastner	„	18.75	„ 26.72	1.2046
F. G.	„	18	„ 26.27	
F. G.	„	21		1.1997
F. G.	„	26		1.2011

The above specific gravities are referred to water at the same temperature as the brine, as far as my own experiments are concerned.

§ 4. *Cold produced on mixing saturated Brine with Water.*—To examine this point, a series of covered beaker-glasses containing known weights of water, and a similar series containing saturated brine, were placed side by side in a tin tray containing water and resting on flannel. The whole arrangement was covered with flannel and allowed to stand over night. In the morning the temperature of eight or ten was found to be exactly  $21^{\circ}$  C. The liquids were prepared by measuring out from a burette in proportions that, taking 1.1997 as the specific gravity of the brine, the ratios by weight were as in columns 3 and 4 (Table I.). The experiments were performed by taking out a water-beaker, rapidly drying its outside, pouring in the brine, stirring with the thermometer, and at once reading.

TABLE I.

Cold produced on mixing saturated Brine with various proportions of Water by weight. Initial temperature  $21^{\circ}$  C.

(1) Water, in grams.	(2) Sat. brine, in grams.	(3) Water, per cent.	(4) NaCl, per cent.	(5) Fall of tempe- rature.
				$^{\circ}$ Cent.
60	140	81.611	18.389	0.4
65	135	82.268	17.732	0.5
70	130	82.925	17.075	0.6
75	125	84.081	15.919	0.75
80	120	84.238	15.762	0.8
85	115	84.895	15.105	0.85
90	110	85.552	14.448	0.9
95	105	86.198	13.802	0.85
100	100	86.870	13.130	0.85
105	95	87.522	12.478	0.85
110	90	88.289	11.821	0.85
115	85	88.835	11.165	0.9
120	80	89.492	10.508	0.9
125	75	90.149	9.851	0.9
130	70	90.806	9.194	0.9
135	65	91.463	8.537	0.75
140	60	92.119	7.881	0.65
145	55	92.776	7.224	0.6
150	50	93.433	6.567	0.6
155	45	94.089	5.911	0.6
160	40	94.746	5.254	0.5

The greatest depression of temperature accordingly in the range of ratio between 84 and 90 of water and 16 and 10 of salt, and the greatest depression of temperature to be got by mixing saturated brine with water, is under no circumstance quite  $1^{\circ}$  C.

§ 5. If now anhydrous salt on dissolving in water absorbs heat only by reason of its conversion into a liquid, and if no hydrate of salt exists at the ordinary temperature above  $0^{\circ}$  C., no such absorption of heat as we have seen to occur could ensue on mixing brine and water. Two series of experiments are therefore at once demanded:—the first to see what proportion must exist between anhydrous salt and water to absorb the most heat; the second to see if at any ratio between salt and water an abnormal change of density takes place.

§ 6. *Cold produced on mixing NaCl with Water.*—A quantity of rock-salt having been finely powdered, was passed through muslin so as to be quite mealy. Various quantities of distilled water were weighed into beakers, and various quantities of the rock-salt were thrown in under constant stirring. The abasement of temperature being noted gave the results of Table II. The temperature of the salt was about  $2^{\circ}$  C. above that of the water.

And it is seen that the greatest abasement of temperature occurs when there is about 40–60 of salt to 160–140 of water (say 25 per cent. of salt). This result is what we should expect, remembering that the saturated solution contains 26·27 per cent. of salt.

TABLE II.—Maximum Cold produced on mixing Salt and Water in different proportions by weight.

Temp. of salt = 20°·2 C.

Water, in grams.	NaCl, in grams.	Temp. of water.	Temp. of mixture.	Fall.
190	10	19·1	18·0	1·0
180	20	18·4	17·0	1·4
160	40	18·4	16·4	2·0
140	60	18·4	16·3	2·1
120	80	18·4	16·5	1·9
100	100	18·5	16·7	1·8

§ 7. *Specific Gravity of Brines of various strengths.*—The question as to the source of cold when brines are diluted can be conveniently approached from an examination of the density of brines of different strengths, and the comparison between the observed specific gravities and the theoretical specific gravities, supposing no change of volume to take place. The brine was found to have a specific gravity of 1·2011 at 26° C., the temperature at which the determinations were made. In Table III. the columns 1 and 2 give the weights in grams of the quantities of water and saturated brine. Columns 3 and 4 give the percentage of the water and NaCl in the resulting brines. Column 5 gives the specific gravity found, and column 6 gives the specific gravity calculated under the hypothesis that no alteration of volume ensues.

TABLE III.—Specific Gravity of Brines of various strengths.

(1) Water, in grams.	(2) Saturated brine, in grams.	(3) Water, per cent.	(4) NaCl, per cent.	(5) Observed spec. grav.	(6) Calculated spec. grav.
0	∞	73·73	26·27	1·2011	
60	140	81·61	18·39	1·1087	1·1328
70	130	82·92	17·07	1·0963	1·1211
80	120	84·24	15·76	1·0874	1·1117
90	110	85·55	14·45	1·0800	1·1014
100	100	86·87	13·13	1·0725	1·0914
110	90	88·29	11·82	1·0650	1·0815
120	80	89·49	10·51	1·0574	1·0718
130	70	90·81	9·19	1·0501	1·0621
140	60	92·12	7·88	1·0428	1·0530
150	50	93·43	6·57	1·0357	1·0434
160	40	94·75	5·25	1·0284	1·0347
170	30	97·06	3·94	1·0246	1·0258



There is accordingly an increase of volume when a solution of salt is diluted; and this is of course connected with the absorption of heat examined in § 4, Table I. When the original temperatures are restored, a mixture of strong brine and water may have a volume two hundredths greater than the sum of the volumes of its constituents. And when the brine contains as little as 4 per cent. of salt, its specific gravity is sensibly smaller than if such a proportion had been the result of the mixture without contraction of the strongest brine and water.

§ 8. *Refraction of Light by Brines of different strengths.*—It seemed, from a consideration of the numbers in Table III., that at or near the point of saturation a definite hydrate of salt exists; and that this is not merely diluted, but also actually decomposed on the addition of water, so that expansion takes place. This I imagined might be tested by the change in the refractive index of the brine. Accordingly brines of various strengths were placed in a hollow prism of  $60^\circ$ . The refraction was measured on a goniometer (Babinet's) table provided with telescope and collimator. An alcohol-flame containing sodium was employed as a source of light shining through a very fine slit. The minimum refraction being obtained, the D line was split by the spider-thread. In Table IV. the empty prism is considered as giving a displacement of  $0^\circ$ . The angular displacements are alone here given, as they perfectly suffice for the detection of singular values.

TABLE IV.

Refraction of Light by Brines of various strengths.

Temp. =  $22^\circ$  C.

Per cent. of brine in solution.	Per cent. of salt in solution.	Displacement.	
$\infty$	26.27	$27^\circ 0' 45''$	or 27.0125
70	18.39	$26^\circ 2' 30''$	„ 26.0416
65	17.07	$25^\circ 44' 0''$	„ 25.7333
60	15.76	$25^\circ 32' 30''$	„ 25.5416
55	14.45	$25^\circ 20' 0''$	„ 25.3333
50	13.13	$25^\circ 10' 0''$	„ 25.1666
45	11.82	$24^\circ 59' 0''$	„ 24.9833
40	10.51	$24^\circ 48' 0''$	„ 24.8000
35	9.19	$24^\circ 37' 30''$	„ 24.6250
30	7.88	$24^\circ 26' 45''$	„ 24.4458
25	6.57	$24^\circ 16' 30''$	„ 24.2750
20	5.25	$24^\circ 6' 0''$	„ 24.1000
0	0.00	$23^\circ 23' 0''$	„ 23.3833

These numbers show a singular value at about the 10- to 11-per-cent. solutions.

§ 9. Another method of attacking the question is offered by the examination of the boiling-points of various brines. Accordingly I took solutions made by mixing saturated brine with water; and waiting for a day on which the barometer stood nearly at the mean, I determined the boiling-points of the brines. The vessels were tall copper cylinders. In the Table V. the temperature of the steam, as well as that of the brine itself, is given. The boiling was, of course, only continued a short time, to avoid the error of strengthening the brine.

TABLE V.

Boiling-points of Brines of various strengths in copper cylinder.

Per cent. of NaCl.	Boiling-point in liquid.	Boiling-point in vapour.
26·27 (sat.)	108·8	107·0
18·389	104·7	104·2
17·075	104·2	103·1
15·762	104·0	102·6
14·448	103·4	102·5
13·130	103·0	102·3
11·821	102·6	101·9
10·508	102·4	102·1
9·194	102·0	101·7
7·881	101·7	101·3
6·567	101·2	101·0
5·254	101·0	101·0
0·00 (dist. water)	100·4	100·0

We have here again a singular value about the 10- to 11-per-cent. solutions.

§ 10. *Freezing-points of Brines of various strengths.*—The molecular separation of water from salt when a brine is boiling has to some extent a counterpart in the separation of ice from brine when the latter is subjected to cold. If a weak brine such as 9 of water to 1 of saturated brine (that is, 1 of salt to 24·2 of water) is subjected to cold, pure ice begins to be formed in this case at  $-1^{\circ}5$ . The temperature gradually sinks; but, as has been shown, the solid part consists of ice, which may be completely freed from salt by mere pressure. This formation of ice continues, and the temperature sinks until the inferior limit attainable by an ice-salt freezing-mixture is reached ( $-22^{\circ}$  C.). The brine, of course, becomes richer and richer in salt. In other words, brines richer in salt yield up ice at lower temperatures. Thus, in Table VI. The same brines are examined as were examined in the preceding Tables. The various brines were examined in succession, being contained in small beaker-glasses in an ice-salt freezing-mixture. It is noteworthy that all

the brines are supersaturable in regard to ice, so that the temperatures are most exactly determined by two observations. A good deal of ice is allowed to form; and this is then suffered nearly entirely to disappear; the temperature is observed at which the ice begins to increase in quantity when the brine is again subjected to cold.

TABLE VI.

Temperatures at which Brines of various strengths give up Ice.

(1) Water, in grams.	(2) Brine, in grams.	(3) Per cent. of NaCl.	(4) Temperature at which ice is first formed.
60	140	18.389	—15.4
70	130	17.075	—15.0
80	120	15.762	—12.4
90	110	14.448	—11.1
100	100	13.130	—9.4
110	90	11.821	—7.7
120	80	10.508	—7.7
130	70	9.194	—6.7
140	60	7.881	—5.4
150	50	6.567	—4.1
160	40	5.254	—3.4
180	20	2.627	—2.1
185	15	1.970	—1.5
190	10	1.313	—1.9 (?)
195	5	0.656	—1.5
200	0	0.000	0.0

Again the brines which contain 10 to 11 per cent. of salt have singular behaviour in regard to the temperature at which they yield ice. These are the very solutions, it will be remembered, which behave singularly in respect of their refractive indices and also of their boiling-points. On comparing with Table III., this singularity does not manifest itself in regard to the specific gravities.

§ 11. *Effect of cooling saturated Brine.*—It is seen from Table VI. that, as far as the strengths of brine there examined extend, the stronger the brine the greater the cold required to separate ice from it. The strongest brine there examined contains 18.389 per cent. of NaCl. If saturated brine (containing 26.27 per cent. of NaCl) be cooled, quite a different class of phenomena ensues. Down to 0° C. no solidification whatever ensues either of ice or of salt. At —7° crystals of the bihydrate are observed to fall ( $\text{NaCl} + 2\text{H}_2\text{O}$ ). These present a beautiful appearance of iridescent scales heavier than the mother-brine. Their composition has been examined by Löwitz, Fuchs, Nölle,

and Mitscherlich, whose analyses, however, are not in good accord, that of Löwitz being as much as 10 per cent. different from the calculated percentage of the bihydrate. Ehrenberg and Frankenheim state that the same hydrate is produced when a dilute solution of chloride of sodium evaporates at  $15^{\circ}$  C., and that it suddenly converts itself into the cubical anhydrous salt and water. At  $-22^{\circ}$  C. the whole of this hydrate appears to be removed. The gradual impoverishment of the mother-brine was tested by maintaining a brine, at first saturated, for half an hour at the successive temperatures  $-10^{\circ}$ ,  $-16^{\circ}$ , and  $-21^{\circ}$  to  $-22^{\circ}$  C. The brine had been previously kept at  $0^{\circ}$  for an hour. The original brine contained 26.2724 of NaCl per cent. It was the mother-brine from each crop of crystals which was subjected to the lower temperature.

		per cent.
Saturated brine at $0^{\circ}$ contained . . . .		26.2724 of NaCl.
Mother-liquor after keeping at $-10^{\circ}$	„	24.6528 „
„ „ $-10^{\circ}$	„	24.6187 „
„ „ $-16^{\circ}$	„	24.1182 „
„ „ $-21^{\circ}$ to $22^{\circ}$		23.8874 „

It is clear, therefore, that down to  $-21^{\circ}$  the solidification impoverishes the brine,—a result which might be due to the formation of the bihydrate or the precipitation of the anhydrous salt, but which is inconsistent with the formation of ice alone. The determinations were made by weighing 10 or 12 grammes of the brines, when at the atmospheric temperature, into long-necked flasks, evaporating and heating to about  $300^{\circ}$  C.

§ 12. A quantity of brine which had been thus impoverished by being kept for an hour at  $-21^{\circ}$  to  $-22^{\circ}$  was decanted into another flask and further cooled by contact with solid carbonic acid and ether. The whole (3 or 4 ounces) solidified; and the temperature remained perfectly constant at  $-22^{\circ}$  to  $-23^{\circ}$  (say  $-23^{\circ}$ ) until the last drop had frozen at  $-23^{\circ}$ ; it then sank rapidly.

If the vessel be continually shaken during crystallization, the form of the crystals may be very clearly seen. While the anhydrous salt crystallizes in the well-known cubes, the bihydrate separates as iridescent scales, and the body we are now considering solidifies in acicular bundles radiating from nuclei, and much resembling in appearance the supersaturated solution of sulphate of sodium when solidifying. It is, however, of a more than pearly whiteness, and finally of complete opacity.

§ 13. To see whether we have here indeed a definite hydrate, the whole was remelted by the warmth of the hand and successively partially refrozen under continual agitation. Each mother-

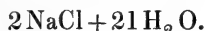
liquor was poured off into a weighed flask and partially solidified, and so on five times in succession. The solid residues were then allowed to melt and get to the temperature of the air; they were then evaporated in the usual way. The portion which remained to the last was not frozen, in order to see whether its composition was the same as that of the parts previously removed by solidification.

TABLE VII.

Percentage of salt in fractionally solidified NaCl brine below  $21^{\circ}$ .

Temperature of solidification.	per cent.
$-21^{\circ}$ to $-22^{\circ}$ , contained	23.7232 of NaCl.
$-22$ "        "	23.6581        "
$-22$ "        "	23.7262        "
$-23$ "        "	23.8201        "
$-23$ "        "	23.3431        "
$-23$ "        "	23.3478        "

The nearest molecular relationship indicated by these numbers is



The formula  $\text{NaCl} + 9\text{H}_2\text{O}$  requires 26.5 per cent. of salt.

"         $\text{NaCl} + 10\text{H}_2\text{O}$         "        24.5        "        "

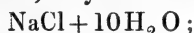
"         $\text{NaCl} + 11\text{H}_2\text{O}$         "        22.4        "        "

"         $2\text{NaCl} + 21\text{H}_2\text{O}$         "        23.6        "        "

§ 14. In these the salient point is the composition of the final mother-liquor, which is essentially the same as that of the successively separated solids.

Accordingly a salt-ice freezing-mixture is just capable of impoverishing saturated brine by withdrawal of salt-rich ingredients (namely the bihydrate) to such an extent that the un-solidified part is homogeneous, in the sense of being solidifiable as a whole. And such solidification takes place immediately below the temperature  $-21^{\circ}$  to  $-22^{\circ}$ , which is the lowest temperature to be got by an ice-salt freezing-mixture. I presume that if the two solids, ice and salt, could be presented to one another in a state of indefinitely fine division, this proportion of 23.6 of salt to 76.4 of ice would act most promptly and continuously as a freezing-mixture, because the formation of the bihydrate would not then occur.

I am disposed to think that the hydrate of salt, the genesis of which is here described, may have the composition



for under the circumstances of its formation and analysis I only see one serious source of error; and that is the condensation of moisture from the air upon the surface of the cold brine. This

would tend to make the amount of salt found too small. To this point we shall have to return.

§ 15. *Physical Condition of a Freezing-mixture.*—The fact that the *rationale* of a freezing-mixture is the liquefaction of solids seems to demand at once the conclusion that a freezing-mixture (of say ice and salt) must always be partially liquid.

Nevertheless, if a mixture be made of about three parts by weight of finely powdered rock-salt and one part of finely crushed ice, the liquefaction which ensues is followed by an apparent regelation so complete that the whole can be handled as a solid mass, and becomes indeed perfectly dry. The cause of this is, I have no doubt, due to the temporary existence of a supersaturated solution of  $\text{NaCl} + 2\text{H}_2\text{O}$ , a body which is formed at about  $-10^\circ$ , Löwitz ( $-5^\circ$ , Nölle) (from  $-3^\circ$  to  $-20^\circ$  continuously, F. G.), when saturated brine is artificially cooled. It is, of course, impracticable to separate this substance from the general mass of the freezing-mixture with sufficient precision to allow of its analysis. The phenomenon of solidification, moreover, only lasts a few minutes. Liquefaction ensues, and the temperature, which had made a pause, again sinks rapidly.

§ 16. The minimum temperature of a salt-ice freezing-mixture seems to be attained between the somewhat wide margins of 3 of salt to 1 of ice, and 1 of salt to 2 of ice. The lowest temperature appears to be  $-21^\circ$  to  $-22^\circ$  C.

§ 17. *Liquid portion of Freezing-mixture.*—It is clear that the liquid portion of a freezing-mixture is a brine of such a composition as to resist solidification at the temperature of the freezing-mixture. Accordingly we ought to find that the liquid portion of a freezing-mixture has the same percentage composition as the mother-liquor of a saturated brine from which the bihydrate has been separated out by the external application of an ice-salt freezing-mixture. To test how far this is verified by experience, dry ice and salt were mingled in three proportions, namely 3 of ice to 1 of salt, 1 of ice to 1 of salt, and 1 of ice to 3 of salt by weight. The salt and ice were in the finest state of division, and the ice was uniformly and as thoroughly dry as possible. The mixtures were constantly stirred in a wooden bowl for ten minutes, and then thrown upon flannel and pressed through.

Ice.	Salt.		NaCl.
3	1	gave a liquid containing	
1	1	„	22·508
1	1	„	24·343
1	3	„	24·711

The amount of salt found is therefore not far off that contained in the 10 hydrate, namely 24·5.

*Cryohydrates.*

§ 18. *General.*—The discovery of the hydrate of chloride of sodium which contains about ten molecules of water to one of the anhydrous salt, caused me to look for similar combinations of water with other salts. This was of course all the more necessary, since if such combinations existed with the salts occurring in the sea, and if such combinations had solidifying-points within the range of the atmospheric temperature, the composition of the solid formed when sea-water freezes would be partly that of ice and partly that of the solid hydrates formed from the brine which had been enriched by the removal of water as ice.

§ 19. It has long been known that the presence of a soluble salt in water depresses the point at which the liquid solidifies (irrespective of the nature of the body separated by solidification). Suppose now we take a solution of the salt *ab* saturated at the ordinary temperature and cool it. We may, above  $0^{\circ}\text{C}.$ , either get a separation of the anhydrous *ab*, or some crystalline combination of the salt with water, a hydrate. To this Na Cl is the only exception; for this body is equally soluble in water at all temperatures above  $0^{\circ}\text{C}.$  Putting Na Cl on one side, we may admit, then, that the mother-liquor gets poorer and poorer as the temperature falls. This is obviously the case if the anhydrous salt falls down; and experience informs us that in order to dissolve a hydrated salt, water, and not the anhydrous salt, must be added. Experience also teaches that there is no marked discontinuity at  $0^{\circ}\text{C}.$  We never find the whole of the salt separated before or even at  $0^{\circ}\text{C}.$  One patent consequence of this is that we can form a freezing-mixture (whereof a portion is liquid) by mixing any soluble salt with ice. We get, therefore, in all cases a solution of the salt below  $0^{\circ}\text{C}.$  If as the temperature is still lowered anhydrous salt were to separate out, we should at last get pure water unfrozen below  $0^{\circ}\text{C}.$ —an impossible result. The same would ensue if a hydrate richer in salt than is the solution were to separate out; whereas if ice or a hydrate poorer in salt than is the solution were to separate out, we should then get at a lower and lower temperature a richer and richer solution, and return to the very condition of strength which the lowering of temperature had altered. This is also an impossibility. Accordingly, in all cases some temperature below  $0^{\circ}\text{C}.$  must be reached at which, after separation of the anhydrous salt or a hydrate richer in salt than the solution, the water and salt solidify together, that is, in constant proportion. The effect of such solidification must be (1) the preservation of a constant temperature during solidification from the moment when the proper proportion between the water and the salt is

reached, and (2) the preservation of that proportion exhibited by the identity of composition of any crop of the solid and the mother-liquor. It is clear that if ice and the hydrated or anhydrous salt separated out in constant proportion and not combined, but merely mixed with one another, the mass would have a constant solidifying- and melting-point; and this would be below zero to the same amount as would be reached on mixing artificially the anhydrous or hydrated salt with ice in the same proportion. But when we have distinct and unchangeable relation by weight demanded by the constancy of the solidifying- and melting-point, we have undoubtedly a numerical physical relation as fixed and no less important than the points of fusion or degrees of solubilities. And if, as I shall show, all the hydrates formed under these conditions have distinct crystalline forms, we have all the conditions of chemical association; at least I know of none other. It is an essential element in the existence of these compounds that they can only exist in the solid state below  $0^{\circ}\text{C}$ . Hence I propose to call them for the present "cryohydrates." At the ordinary temperatures they melt in their own water of crystallization, and appear as ordinary solutions never saturated. And when once the proportion between the salt and the water in a cryohydrate has been found, the cryohydrate can be formed in any quantity by dissolving the salt in water in the required proportion. Such a solution shows no sign of yielding up ice or anhydrous salt (or other hydrate) until its temperature, on being lowered, reaches a certain temperature peculiar to the salt (unless under supersaturation); it then solidifies as a whole, maintaining throughout that constant temperature. Above this temperature (that is, in the melted state) it is precisely in the same predicament as a salt melted in its own water of crystallization.

§ 20. The same cryohydrates are (and indeed must inevitably be) formed if we cool such a solution of the respective salt in water as contains a greater proportion of water than the cryohydrate. As we have seen in §§ 10, 13, where the experiments dealt with brine of  $\text{NaCl}$ , ice is then formed, and the liquid gets richer and richer in salt, falling in temperature till the ratio proper to the cryohydrate is reached; whereupon, as before, homogeneous solidification ensues without abasement of temperature. If we approach the cryohydrates from this side (that is, by removing ice from a dilute solution), we are sure not to run the risk of being inconvenienced by the intervention of any intermediate hydrate similar to the bihydrate of chloride of sodium (§ 11). But such intermediate hydrates are of the rarest possible occurrence; so that, on account of the high specific and latent heat of water, it is invariably most convenient to start from a saturated solution.

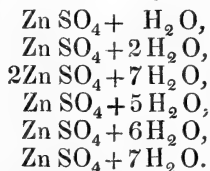


§ 21. *Cryohydrate of Chloride of Ammonium*.—A saturated solution of  $\text{NH}_4\text{Cl}$  was cooled in ice and the liquid portion transferred to a beaker surrounded by an ice-salt freezing-mixture. The temperature fell continuously, and anhydrous chloride of ammonium kept falling down. At  $-15^\circ$  the solidifying part presented a different appearance. It then took the form of a brilliant white apparently flocculent mass lighter than the unsolidified liquid. After standing, with stirring, for a quarter of an hour, the temperature was still  $-15^\circ$ . The clear portion was poured off into a fresh beaker, to which the cold was applied. The solidifying parts are now seen to be minute crystals, very much resembling ice-flowers, but opaque. The sides of the beaker become studded with transparent crystals of four sides, which are striated parallel to the sides. By and by these crystals become perfectly white and opaque, and a third axis of crystallization is developed, which was at first suppressed. The crystals are perfectly beautiful, resembling, where opaque, frosted silver. On allowing a thick cup to freeze and breaking it, an exquisite pearly appearance is presented. The structure appears then quite fibrous, the fibres running perpendicular to the axis of the cup; and the appearance, as far as structure is concerned, is similar to that of sublimed chloride of ammonium. The temperature remains constant at  $-15^\circ \text{C.}$ , even to perfect dryness. The first crops of crystals were rejected as being possibly contaminated with  $\text{NH}_4\text{Cl}$ . The last crop and the mother-liquor were analyzed by being weighed into glass basins and evaporated at  $100^\circ \text{C.}$

	grms.	$\text{NH}_4\text{Cl}$ .	per cent.
I. . . .	9.5360	gave 1.7573,	or 18.43
M.L. II. . . .	6.0890	„ 1.1895	„ 19.56

The analysis II., which is of the mother-liquor, corresponds nearly with the molecular relation  $\text{NH}_4\text{Cl} + 12\text{H}_2\text{O}$ , which requires 19.98 per cent. of  $\text{NH}_4\text{Cl}$ .

§ 22. *Cryohydrate of Sulphate of Zinc*.—The hydrates of sulphate of zinc already known are very numerous. They are :—

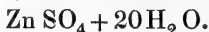


The last, which is the ordinary form of zinc-vitriol, when saturating water at  $17.5^\circ \text{C.}$ , gives a solution, according to Karsten, consisting of 52 per cent. of salt and 48 per cent. of water. On cooling such a solution to and below  $0^\circ \text{C.}$ , the heptahydrate

crystallizes out; and this, consisting of 56 of salt to 44 of water, impoverishes the mother-liquor until the latter contains 30·84 per cent. of the anhydrous sulphate. The temperature is now  $-7^{\circ}\text{C}.$ , and it remains constant at this degree. The last fraction having solidified at this temperature, was remelted and the water estimated by evaporation and heating to  $240^{\circ}\text{C}.$

8·1531 grms. contained 2·5146 grms. of  $\text{Zn SO}_4$ ,  
or 30·84 per cent.

This corresponds very closely with the composition



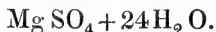
It is noteworthy that this cryohydrate, after standing some days in a hermetically sealed tube, deposits massive rhombic crystals and a fine powder. I have not analyzed these; they are possibly the monohydrate and one of the intermediate hydrates insoluble in the fused cryohydrate.

§ 23. *Cryohydrate of Sulphate of Magnesium.*—Combinations are known consisting of 1 molecule of sulphate of magnesium combined with 1, 2, 6, 7, and 12 molecules of water. The last is the more interesting because Fritsche describes its formation from a saturated solution of the sulphate when cooled below  $0^{\circ}\text{C}.$  I find that when a saturated solution is cooled to  $-5^{\circ}\text{C}.$  and transferred to a clean vessel, it may, if perfectly free from crystals of the 7-hydrate, be cooled to  $-10^{\circ}\text{C}.$  without any further solidification. As soon, however, as further cold causes crystallization, the temperature rises to  $-6^{\circ}\text{C}.$ , and remains constant at this point during the whole of the subsequent solidification, provided that a crystal of the previous crop is put into the cooled mother-liquor after each decantation.

The composition was determined by heating to  $240^{\circ}\text{C}.$

7·6564 grms. gave 1·6736 gm. of anhydrous sulphate,  
or 21·86 per cent.

This corresponds to 23·83 (say 24) molecules of water. Its molecular ratio seems therefore to be

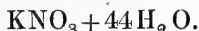


§ 24. *Cryohydrate of Nitrate of Potassium.*—As far as I can inform myself, nitre, like the chloride of ammonium, has not hitherto been combined with water. The solution saturated at  $20^{\circ}\text{C}.$  gives an abundant crop of nitre at  $0^{\circ}\text{C}.$  There appears to be no intermediate hydrate, the body which separates at  $-2^{\circ}5\text{C}.$  being apparently pure nitre. At  $-2^{\circ}7$  another body is formed, whose crystalline form resembles ice. It adheres to the side of the vessel; when separated, it floats, being lighter than the mother-liquor at  $-2^{\circ}7$ ; but when thrown into water at  $20^{\circ}\text{C}.$ , it sinks, showing that it is not ice. The last four crops

of crystals were analyzed. The final one was formed also exactly at  $-2^{\circ}7$ .

	Liquid.	KNO <sub>3</sub> .	per cent.
(1)	8·8030	gave 0·9221	or 10·4
(2)	1·6709	„ 0·1959	„ 11·7
(3)	3·0300	„ 0·3350	„ 11·06
(4)	4·2280	„ 0·4770	„ 11·2

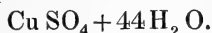
The molecular relation is therefore about 1 : 44·6.



§ 25. *Cryohydrate of Sulphate of Copper*.—The ordinary hydrates of blue vitriol are the mono-, bi-, and pentahydrates. On cooling a saturated solution, the constant temperature of solidification is found to be  $-2^{\circ}\text{C}$ . The last crop of crystals being remelted, was evaporated and heated to the anhydrous state.

6·6952 grms. gave 1·1312 grm.  $\text{CuSO}_4$ , or 16·89 per cent.

This corresponds to the atomic relation of 1 : 43·7 (say 1 to 44)

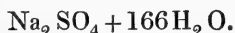


Each crop of crystals, when melted, and the mother-liquor present identically the same depth of colour.

§ 26. *Cryohydrate of Sulphate of Sodium*.—A very great many ordinary hydrates of this salt are known. I find that a saturated solution has a solidifying-point at  $-0^{\circ}7\text{C}$ .

4·0630 grms. contained 1·850 grm. of  $\text{Na}^2\text{SO}_4$ ,  
or 4·55 per cent.,

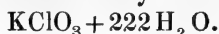
corresponding to the molecular ratio of 1 : 165·6 (say 1 to 166),



§ 27. *Cryohydrate of Chlorate of Potassium*.—The chlorate of potassium, like the nitrate, has not hitherto been combined with water. Almost the whole of the salt separates out in the anhydrous state when a saturated solution is cooled to  $0^{\circ}\text{C}$ . On further cooling to  $-3^{\circ}\text{C}$ ., the solution may present a remarkable condition of double supersaturation. If at this temperature a crystal of anhydrous chlorate is dropped in, anhydrous chlorate is formed in considerable quantity. If an ice fragment is introduced, ice only is formed. If both are thrown in, both are formed, the one set of crystals floating, the other sinking. If the temperature of the supersaturated solution be further cooled, the proper cryohydrate separates out and the temperature rises to  $-0^{\circ}5$ . The normal formation ensues on introducing a crystal of the cryohydrate from one crop to start the formation of the next. This phenomenon, which is not without its counterpart in some other cases, argues forcibly for the existence of a distinct crystalline form proper to the cryohydrate.

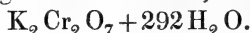
- (1) 13.2512 grms. of cryohydrate gave 0.3912 grm.  $\text{KClO}_3$ ,  
or 2.95 per cent.  
(2) 13.5810 grms. of cryohydrate gave 0.3915 grm.  $\text{KClO}_3$ ,  
or 2.88 per cent.

The molecular relation is exactly



§ 28. *Cryohydrate of Bichromate of Potassium*.—I chose this salt because it is not constructed on the ordinary salt type. I found it solidified entirely at  $-1^\circ \text{C}$ . The crystals, which are at first transparent, become opaque, and are of a bright straw-yellow. 5.4968 grms. gave 0.2868  $\text{K}_2\text{Cr}_2\text{O}_7$ , or 5.305 per cent.

This gives the largest ratio of water, namely



As with the sulphate of copper, so in this case all crops of crystals, when melted, had exactly the same depth of colour.

§ 29. *Sources of error*.—I need scarcely point out that the molecular ratios derived from the above experiments can only be considered provisional. In the case of bodies which combine with as many as forty and upwards molecules of water, a very slight error in the determination may make a difference of one or two molecules of water. In those which have a very low solidifying-point, another source of error creeps in. The liquids, even on pouring from one vessel to another, dilute themselves by condensing moisture from the air. With due regard to the probable direction of error in each case, I venture to submit the following tabulation, showing in column 1 the anhydrous salt, in 2 the temperature Centigrade of solidification, in 3 the actual percentage of anhydrous salt found, and in 4 the number of molecules of water to one of salt.

TABLE VIII.

Temperature of Solidification and Molecular Ratio of Cryohydrates.

(1)	(2)	(3)	(4)
	Temp. Cent.	Per cent. of salt.	Molecules of water to 1 of salt.
$\text{NaCl}$ .....	$-23^{\circ}$	23.603	10.5(? 10)
$\text{NH}_4\text{Cl}$ .....	$-15$	19.56	12.0
$\text{ZnSO}_4$ .....	$-7$	30.84	20.0
$\text{MgSO}_4$ .....	$-6$	21.86	24.0
$\text{KNO}_3$ .....	$-2.7$	11.20	44.0
$\text{CuSO}_4$ .....	$-2$	16.89	44.0
$\text{Na}_2\text{SO}_4$ .....	$-0.7$	4.55	166.0
$\text{KClO}_3$ .....	$-0.5$	2.93	222.0
$(\text{K}_2\text{Cu}_2\text{O}_7)$ .....	$-1.0$	5.306	292.0)

§ 30. The above are arranged according to the molecular ratio, NaCl having the least number of molecules of water. At once an important law declares itself: those cryohydrates which have the lowest solidifying temperatures have the fewest molecules of water. This law holds true with all which have been examined, with the exception of the bichromate of potassium, which, if placed according to its temperature of solidification, would be above the sulphate of sodium. Is this due to its abnormal composition? Such questions suggest themselves by the score on contemplating this Table VIII.

§ 31. I have found the solidifying-points, and have hermetically sealed specimens, of the cryohydrates of a few other salts, and am collecting more previous to analyzing them. I give their solidifying-points in the order of the degree of cold; and it will be of great interest to see whether their molecular ratios fall in accord with the above rule.

Salt.	Solidifying temperature of cryohydrate.
KI . . . . .	—23·0
KBr . . . . .	—13·0
KCl . . . . .	—11·4
Na <sub>2</sub> CO <sub>3</sub> . . . . .	— 2·0
Ba NO <sub>3</sub> . . . . .	— 0·8
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . . . . .	— 0·5

Perhaps the most promising direction of inquiry for the establishment of such a uniformity of result as may be used for the prediction of untried experiments will consist in a careful study of the nine salts between K, Na, and NH<sub>4</sub> on the one hand, and Cl, Br, and I on the other.

#### *Some Experiments with Sea-water.*

§ 32. *Freezing sea-water.*—The sea-water with which the following experiments were performed was procured from Dover. After filtration, it was found to have at 760 millims. the boiling-point 100°·6, while the temperature of its vapour was 100°·2. This sea-water began to freeze at —2° C. On evaporation on a water-bath and keeping at 100° C. for two hours, the percentage of solid residue was 6·5786. A large beaker of this sea-water was cooled to 0° C. A tin vessel was supported inside the beaker so that its bottom just touched the surface of the water; and a freezing-mixture was placed in the tin vessel. When about  $\frac{1}{100}$  of the whole had solidified, the solid was removed and divided into two parts: one was allowed to melt, and its percentage of solid matter was determined as above; the other was broken up and frequently pressed between linen and flannel in a screw press, being allowed to melt as little as possible. The percentage of

solid matter in this also was determined. The following numbers show the result of this examination :—

	Per cent. at 100° of solid residue.
Sea-water . . . . .	6·5786
Frozen sea-water . . . . .	5·4209
Frozen and pressed sea-water . . . . .	0·4925

It appears, then, that under these conditions the freezing of sea-water is little more than the freezing of ice, and that the almost undiminished saltiness of the unpressed ice is due, as suggested by Dr. Rae, to the entanglement amidst the ice-crystals of a brine richer in solid constituents than the original water itself. Such brine, which is here squeezed out in the press, drains in nature down from the upper surface of the ice-floe by gravitation, and also is replaced by osmic action by new sea-water which again yields up fresh ice; so that while new floes are porous and salt, old ones are more compact and much fresher, as the traveller observed.

§ 33. But, bearing in mind the existence of the cryohydrates, certainly of sulphate of magnesium and doubtless also of chloride of calcium at temperatures not far below 0° C., a rapid fall of temperature may be accompanied by more complex phenomena of gelation; for if the ice be quickly removed from a large mass of water by freezing, the resulting brine may easily be so enriched as to throw out one or more cryohydrates, which thus perpetuate *in situ* a definite amount of saline matter. How far such cryohydrates are soluble in the chief cryohydrate, namely that of NaCl, which by itself resists the cold the longest, is an important matter for future research. But there can even, viewed in the light of the experiments given above, be little doubt that the degree of saltiness of a floe depends not only upon its age, but also upon the rapidity with which it was at first formed, and upon the lowest temperature to which it has subsequently been exposed.

§ 34. Since sea-water has no maximum density below its freezing-point, when a mass of sea-water is uniformly cooled to  $-2^{\circ}$  C. ice will be formed at any point, whether at the bottom or at the surface, which loses more heat. Even the middle of a mass of sea-water may lose heat by radiation, and crystals of ice be thus formed in the mass. Or the bottom of the sea may radiate sufficient heat through the ice-cold layers above to freeze the water in contact with it, and thus generate large masses of ice which break off and carry with them parts of the sea-bottom. But I suppose the ice of the sea is mainly formed at or near the surface by radiation from the surface into space and by contact with the colder air. To imitate as nearly as I could the condition which I suppose to exist, I

cooled the sea-water to  $-2^{\circ}$  C. in a beaker, which I enveloped thickly with flannel. I tried in vain to freeze the surface by blowing over it dry air which had passed immediately before through a long pewter worm immersed in a freezing-mixture. But I succeeded in getting a sheet of ice when I hung a freezing-mixture contained in a blackened tin pan within about  $\frac{1}{8}$  inch of the surface of the water, the whole being plentifully enveloped in flannel. Perhaps here the actual conditions which obtain when sea-water freezes were reproduced. I found that the pressed ice contained only 0.4052 of solid residue at  $100^{\circ}$  C.

§ 35. The question suggested itself to me whether, when one part of a solution of a salt is cooled, there may not be an accumulation of salt in the cooler part, although not accompanied by any solid separation. I accordingly cooled a saturated solution of nitre to  $-1^{\circ}$  C. and decanted from the separated nitre. I then warmed the solution in a tall beaker-glass to  $60^{\circ}$  C. and placed the bottom of the beaker in melting ice. In an hour's time a thermometer at the bottom stood at  $10^{\circ}$  C., at the top at  $33^{\circ}$ . A specimen from the bottom contained 11.3 per cent. of nitre; one from the top contained 11.7 per cent. of nitre—showing that there was no sensible diffusion of the salt one way or the other.

#### *General Considerations.*

§ 36. *Maximum density of Water.*—It was shown that brines of various strength, when mixed with water, absorbed heat and expanded. Let us look upon ice as the cryohydrate of water. Water shrinks as it loses heat till it reaches  $4^{\circ}$  C. At this point ice is formed, which, however, is dissolved in the water. A solution is obtained having a temperature of solidification below  $4^{\circ}$  C., namely at  $0^{\circ}$  C. At  $0^{\circ}$  C. the ice and the water solidify together, producing the compound body or cryohydrate called ice, which is thus a cryohydrate of water. The expansion from  $4^{\circ}$  to  $0^{\circ}$  is due to the greater and greater amount of ice which the water holds in solution, and which expansion is greater than the contraction of the water due to the diminished temperature.

§ 37. *Variation of media.*—There can be no doubt that the discovery of an enormous number of new bodies of definite composition will reward those who labour in this field. Taking water as the medium for solution, there appears to be no doubt that every soluble salt has a definite cryohydrate; so that in this direction alone the number of new bodies awaiting discovery and description may be estimated at half the number of bodies already known. If we vary the medium, employing, say, alcohols or hydrocarbons as solvents, the number of new compounds will be again indefinitely increased; so that it is fairly within the

truth to assert that the number of known bodies may soon be doubled.

§ 38. *Geological*.—The behaviour of mixtures of salts will again offer a new chapter for study; and I suppose we may expect that much light will be thus thrown upon some of the most obscure geological questions. For though we have been considering above cryohydrates (that is, compounds of water solidifying below the freezing-point of water), there can be no discontinuity separating the medium water with its peculiar temperature of solidification from other media of very different melting-points. We know already, indeed, very many instances in which the mixture of two bodies has a lower melting-point than either of its constituents. What must happen, then, if a mass of molten rock, such as a silicate, is saturated at a high temperature with another silicate? When the mixture cools, the second may separate out in the solid form, perhaps as quartz, perhaps as felspar, or what not. Anon, at a certain lower temperature, solidification takes place between the medium and the dissolved rock in definite proportion—definite, though perhaps not necessarily in chemical ratio, but presenting that mineralogical ratio which is so striking, and which has not hitherto been satisfactorily explained.

§ 39. *Constant temperatures*.—Perhaps one of the most interesting aspects of the experimental results is the establishment of fixed temperatures below zero. With the exception of the melting-points of a few organic bodies such as benzol, and the boiling-points of a few liquids such as liquid ammonia, sulphurous acid, and carbonic acid, and the rather ill-defined temperatures to be got by various freezing-mixtures, there are no means in the hands of physicists for obtaining and maintaining with certainty and ease a fixed temperature below  $0^{\circ}\text{C}$ . Now, if we surround a body with one of the solid cryohydrates described above, the body is kept at a corresponding temperature as long as any of the cryohydrate remains solid, and this with as much certainty as the temperature  $0^{\circ}\text{C}$ . can be maintained by melting ice. We thus command temperatures between  $-23^{\circ}$  and  $0^{\circ}\text{C}$ . with the greatest precision.

§ 40. *Invitation to others*.—I need scarcely point out that the field of inquiry which has been here opened is far too large to be satisfactorily examined by one worker. It is notably at the commencement that the collaboration of many workers is most beneficial, so that fundamental errors may be quickly corrected. On this ground I respectfully invite my fellow-labourers to this branch of inquiry.

I have received through a considerable part of this inquiry much valuable assistance from my friend Mr. F. H. Marshall.



## II. On Aniline Derivatives.

By EDMUND J. MILLS., D.Sc., F.R.S.\*

THE following results in connexion with aniline derivatives were obtained during the course of an investigation for which the substances that will be referred to were required.

*Separation.*—When chloraniline, bromaniline, &c. are prepared by acting on an anilide with chlorine &c., the function has usually a double period; so that mono-, di-, and tri-derivatives are generated in presence of each other. In order to separate these I proceed as follows. The mixed derivatives are immersed in a very large excess of aqueous hydric chloride (1 vol. common fuming chloride to 9 vols. water) and heated to nearly 100°, with frequent stirring, for about an hour in a loosely covered vessel; the whole is then allowed to cool down until the next day. The clear liquid contains only mono- and di-derivatives, the insoluble portion di- and tri-derivatives. The latter is submitted to repeated hydrochloric treatment as before, until the supernatant clear liquid no longer gives any precipitate with ammonia; it then consists of tri-derivative only—contaminated, indeed, with some black tarry products. This derivative can be purified by distillation *per se*, or from strong aqueous hydric chloride or potash-lime. The clear liquids are united and precipitated with ammonia during twenty-four hours, a large excess of ammonia being avoided. The precipitate is then washed, rapidly evaporated with hydric chloride to dryness on the water-bath, redissolved (or at any rate well stirred) in hot water, and left to cool thoroughly: the insoluble portion consists of di-derivative, and must be filtered off. The filtrate is again evaporated to dryness and stirred with hot water &c. Three evaporations to dryness are necessary, and usually sufficient; and the final solution contains mono-derivative only, which yields but an inappreciably small amount of insoluble residue when so evaporated. The mono-derivative can be purified by distillation from aqueous soda in a current of steam; the di-derivative by distillation *per se*, or by successive crystallizations from naphtha and spirit.

When aniline is intended to be converted into chlorine, bromine, or iodine derivatives, it should be dried and purified by cohobation for a few hours with about one eighth to one sixteenth of its weight of mercuric chloride, bromide, or iodide respectively. Subsequent fractional distillation easily furnishes a very pure product. Only aniline so purified is referred to in the following experiments.

*Preparation.*—(α) Aniline is cohobated with glacial hydric

\* Communicated by the Author.

acetate for some hours so as to form acetanilide, which is then purified by crystallization. The acetanilide is powdered, suspended in water, and treated with excess of bromine or chlorine (Proc. Roy. Soc. vol. x. p. 589): the product is heated with powdered potash, moistened with spirit. This method gives good results. The product consists chiefly of mono- and tri- derivatives.

(β) It is not necessary to prepare acetanilide; a solution of dry aniline in glacial acetate answers equally well. Aniline is dissolved in 2–3 vols. of acetate, and chlorine- or bromine-vapour passed over the surface of the mixture, which must be well agitated. [In the case of bromine-vapour, the operation is performed in a warm closet, and the bromine is volatilized slowly from a retort, which must be heated by a small flame placed a considerable distance below. It is very easy thus to manage so that, while vapour comes over freely, no drops of bromine are delivered from the tube of the retort. This tube should be bent vertically downwards, and nearly touch the surface of the aniline mixture in the flask where the operation is conducted.] Considerable heat is evolved at first. As the reaction proceeds, the mixture becomes thicker, and partially solidifies; and at this point the operator will arrest it if he requires a minimum of tri- derivative, but continue until total solidification ensues if he wishes the tri- derivative to be a maximum. The whole may, if desired, be again submitted to further action by gently heating with more glacial acetate, which causes solution to occur. The cooled mass is heated to 100° under water, and afterwards cooled therewith. The supernatant liquid is filtered off and precipitated with alkali: this precipitate contains mono- and di- derivatives. The insoluble portion is mixed with powdered potash, moistened with spirit, and then heated in order to destroy any traces of anilide that may have been formed. The three derivatives are separated from the dark mass as already stated. The distinguishing feature of this mode of reaction is, that it is completely under the control of the experimenter. The ratio  $C^8H^9ON : Br^2$  furnishes chiefly dibromaniline. Doubtless this process applies to other amines.

(γ) The direct action of chlorine &c. on aniline itself is not attended with satisfactory results; in presence also of water or aqueous hydric salt there is an enormous amount of by-product. Aniline purified by distillation with mercuric iodide yields exceedingly little moniodaniline.

(δ) Aniline may be mixed with plumbic oxide, and iodine &c. added\*. I have only succeeded in preparing traces of iodaniline in this way. A considerable amount of crude product is obtained,

\* This is Stenhouse's method of iodating orcin.

but it is difficult to purify. The only substance I was able to separate, in two large operations, was volatile in a current of steam, white, and crystalline; it was soluble in aqueous hydric chloride, and precipitated therefrom by ammonia, but not by platinic chloride after repeated crystallization from spirit. When melted, it gave no definite fusion-point.

*Properties.*—Having contrived a very delicate apparatus for the determination of fusion-point, I have been enabled to make some interesting comparisons among these derivatives; but the actual numbers (though otherwise completely corrected) have not yet been converted into degrees of the air-thermometer. All the determinations are made upon substances repeatedly purified by fractional methods; and in no case is the probable error of the fusion-point greater than  $0^{\circ}01$ . The result of fifty-five observations with monochloraniline from acetanilide was  $69^{\circ}69$ ;  $0^{\circ}03$  higher than that of forty-eight observations with the derivative of the direct acetic process. Dichloraniline could not be obtained in sufficient quantity for systematic examination by either of the methods ( $\beta$ ) or ( $\gamma$ ).

Trichloraniline was very easily made by the direct acetic process, and purified by distillation in a current of steam. The anilide process yields little, if any. For the organic analysis of this substance I am indebted to the kind offices of my friend Mr. Valentin.

0.3392 grm. substance gave 0.7486 grm. argentic chloride.

0.2311 grm. of the same substance gave 0.3103 grm. carbonic dioxide.

0.2758 grm. of the same substance furnished 0.3690 grm. carbonic dioxide and 0.0600 grm. water.

	Found.	Calculated.
Argentic chloride . . .	220.7	219.1
Carbonic dioxide . . .	134.3, 133.8	134.4
Water . . . . .	21.7	18.3

These numbers agree very well with theory. The fusion-point, as determined by ninety-six observations with two mercurial thermometers, was  $77^{\circ}05$ ; and it occurs so sharply, that the probable error of the result is only  $0^{\circ}0014$ . Lesimple (*Ann. Chem. und Pharm.* vol. cxxxvii. pp. 126 & 127) describes a trichloraniline which he obtained by reducing nitrotrichlorobenzol. He states that it has a very unpleasant and persistent smell, and that it melts at  $96^{\circ}5$ . On these two points my derivative differs from his: it has rather a faint odour, but not very unpleasant, and melts  $19^{\circ}$  lower. In all the other reactions mentioned by Lesimple the two bodies exhibit a complete agreement.

Monobromaniline prepared from acetanilide melted at  $61^{\circ}80$

(69 obs., two thermometers); the direct process gave  $61^{\circ}85$  (28 obs., one thermometer). Dibromaniline was prepared as stated above ( $\beta$ ): the direct acetic process yielded me little, if any, with the same ratio of reagents. The fusion-point was  $78^{\circ}82$  (100 obs., two thermometers). Tribromaniline from acetanilide melted at  $116^{\circ}22$  (30 obs., one thermometer); that which was made by the direct acetic process melted at  $116^{\circ}28$  (42 obs., two thermometers).

From purified aniline only a very minute amount of moniodaniline was obtained by three trials of a direct action in the ratio  $2C^6H^7N : I^2$ . In presence of plumbic oxide ( $C^6H^7N : I^2 : \frac{PbO}{2}$ )

the yield was rather greater; but the fusion-point of the portion volatile in steam gradually rose on repeated crystallization to  $86^{\circ}$  and beyond, with no certain indication of a settlement. This product appeared to contain traces of ordinary moniodaniline; but after the final crystallization it yielded no platinic salt insoluble in alcohol and ether. The residue in the retort, non-volatile in steam in presence of potash, contained aminic bodies soluble in dilute aqueous hydric chloride. These are perhaps the missing poly-iodanilines.

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### III. *Carbon and Hydrocarbon in the Modern Spectroscope.*

*By PIAZZI SMYTH, Astronomer Royal for Scotland\*.*

[With Two Plates.]

IN the November Number of the Philosophical Magazine appears a paper "On the Spectrum of Carbon," by an author whose name is well known and widely respected both in spectroscopic inquiries in general, and carbonaceous spectra in particular, viz. W. Marshall Watts, D.Sc. Yet there would seem to be a something somewhere wanting in the said paper if it is to represent the state of knowledge in 1874 rather than 1854, and to lead towards the discovery of truth as it is in nature.

The author sets out by suggesting what he considers an improved method for astronomers in observing the rather puzzling spectra of comets, viz. "to work by eye-estimations of the distance of the bands from the known bands of some equally faint spectrum, made to occupy the lower portion of the field of view, provided," says he, "a faint spectrum can be found *possessing a sufficient number of well-defined bands in the region of the spectrum*

\* Communicated by the Author.

*to be mapped.*" This, as italicized by him, is very clear; and he finds such a reference in what *he* calls the carbon-spectrum, but which others before him, whom he does not mention, have called the spectrum of carbohydrogen, of acetylene, of marsh-gas, and of general blue base of flame.

Impressed next with the importance of the places of the bands of that spectrum being known to great accuracy, Dr. Watts proceeds to give his own recent, and doubtless very good, measures of the wave-lengths of certain fine lines therein, and concludes with stating what substance the whole collection is the spectrum of, and what it is not, both in chemistry and physics.

*The principle involved.*

Now to the principle of spectroscopic observation announced in the first part of the paper I certainly cannot object, seeing that it is, step by step, the very method and the very reference-spectrum which I have been employing for four years past, and am still using in this royal observatory, and have often published upon, hoping to promote its general adoption. My first attempt indeed was not very successful; for having sent a paper on the subject to the Royal Astronomical Society on May 30, 1871, with the request that it might be read at the next meeting and printed in the following 'Monthly Notices,' that learned body (which is a very excellent body except in so far as it deals in the accursed thing for all free countries, of *secret* committees) chose to keep my paper back for six months without rendering any reason why.

However, I having met, during those months, with Professor Swan of St. Andrews, who first accurately measured that spectrum's lines, so far back too as in 1856—and I having held forth to him on the delightful and universal reference for faint astronomical spectra which I had found in that chemical spectrum which he had previously made so peculiarly his own, both by a priority without any question, and an accuracy which Professor Kirchhoff has since then pronounced to be classical,—he was induced to go to Section A of the British Association, then meeting in Edinburgh, and gave them a good and sound paper on the subject, besides furnishing me with his own special reductions of some of his angles of the refractive indices of the lines into wave-lengths, agreeably with Angström's normal solar spectrum.

Afterwards, too, I not only printed the so-long-stopped paper in the thirteenth volume of the Astronomical Observations of the Royal Observatory, Edinburgh (together with Professor Swan's wave-lengths as above), but in the beginning of 1872 practised the method still further on the zodiacal light at Palermo, and on

twilight and phosphorescence in many seas, and then sent a second paper to the Royal Astronomical Society. And that one they did print in the same year, with a very good engraving, too, of my several pairs of spectra just as they were simultaneously seen in my spectroscope—one member of each such pair being, for reference sake, invariably the bands and lines of the carbon- or hydrocarbon-spectrum, precisely as Dr. Watts is now proposing it in 1874, and as, too, I have since found that it was used before my time in telespectroscopy by the eminent Lewis M. Rutherford, of New York, and differing only in the manner of producing the spectrum from what Dr. Huggins actually accomplished on the comet of 1866 and on several others since then.

Truly, therefore, I have nothing to say against the principle of the method proposed now by Dr. Watts as his own; but I am sorry to differ from him in the instrumental description which he gives of the visible spectrum concerned, and which will affect the observations of all persons who use it as a standard of reference.

#### *Mensuration of the Spectrum referred to.*

The Doctor remarks, sagely enough, that for cometary work the reference-spectrum should be of “feeble intensity;” why then does he not examine it in that shape, viz. as given by the blue base of the flame of a small alcohol lamp, or the all but vanishing globule of flame when a common gas-light is on the point of going out from inanition?

But in place of so doing, he takes brilliant olefiant gas and burns it with oxygen “at the platinum nozzle of an oxyhydrogen blowpipe.”

That in itself is quite enough to introduce some variations in the spectrum of a volatile chemical compound; and he gets still more when he examines it, not under the small dispersion usually employed on comets, but with the tremendous dispersion of six dense flint prisms. For to such an overpowerful instrument the appearance of the several “bands” (which is the characteristic feature under small dispersion) is almost annihilated, being replaced by more or fewer of the successive and almost isolated lines of which those bands are ultimately composed in nature, but which fine lines no one has ever seen, or need expect to see, in the spectrum of any ordinary comet.

The first step, therefore, in the Doctor’s instructions to astronomers might well have been on the “bands,” and should have been very complete with them; what will not, therefore, be any one’s surprise to find that though the spectrum in question consists notably and notoriously (even when prepared from

sources of most feeble intensity) of *five* bands, viz. the orange, citron, green, blue, and violet, yet Dr. Watts, though from his intense (and even oxygen-excited) spectrum, indicates the existence of only three out of those five.

These three, which are really the citron, the green, and the blue, he names  $\gamma$ ,  $\delta$ , and  $\epsilon$  rather confusingly; for in such case any one will ask, "where are the  $\alpha$  and  $\beta$  of the system?" They are nowhere in the Doctor's paper of 1874; and even in his book of 1872, a very useful little book ('The Index of Spectra'), and where  $\alpha$  does appear as the orange group, there is no  $\beta$ , and the violet band is most annoyingly called, among so many Greek letters, by the italic *h*, and there are many other lines only seen when oxygen and various other elements are used extravagantly.

But letters, whether Greek or Roman, are sadly misplaced in their application to coloured "bands." They are not needed, because the names of the colours describe such bands, and their places, better; and Greek letters have been already appropriated to the bright *lines* of luminous and discontinuous spectra, in whose range they appear then consistently with the application of the same Greek letters to the brighter stars in any constellation, but never as a designation of a whole constellation of stars.

To make this point (of what are the bands and what are the lines) clear, I beg to introduce my present working diagram of the spectrum as a reference in astronomy (Plate I.); and while it will be seen that the "bands" are distinguished by the names of their colours, the lines in each band are distinguished by the numbers of their wave-lengths, precisely as Dr. Watts distinguishes them in his new paper of 1874; while they are also distinguished further in nature, and my drawings, by the brightest of each band being on the less-refrangible side, and going off gradually into invisibility on the more-refrangible side.

(And here I crave permission to write a rather long parenthesis, on a tangle needlessly introduced into the printed accounts of this spectrum, thus. As there is no allusion in the paper of 1874 to the Doctor's more important work of 1872 being cancelled, it remains as an authority, a competing authority, too, with the paper; whence, on putting the two side by side this singular discrepancy of terms comes out—viz. that the book calls "groups" what the paper calls "bands," the book again calling "bands" what the paper calls "lines," while finally the book calls "lines" some finer and intercalated modifications still, not mentioned in the paper at all. But the book does not venture to give the wave-length places of these extra-fine and interstitial lines belonging to it alone; and as they are certainly not

to be seen with all ordinary and some extraordinary forms of spectroscopes in any usual and convenient formula for preparing the carbohydrogen-spectrum of a moderate intensity, I propose not to take any further account of them now, except to say that, if I ever do meet them in future spectroscopy, I shall probably call them "linelets," or some such diminutive of lines, leaving therefore our present arrangement, and also Dr. Watts's present-paper arrangement, of bands and lines intact.)

Of these last most proper lines, then (in any ordinary spectroscope with a fine slit), let us speak now touching their appearance in Dr. Watts's new-paper account of them for 1874. They are given there as though they had never been observed or measured by any one else previously; and no one is entitled to object much to that, if they are now set forth in a better and completer manner (especially for the practical use of astronomers) than in all former accounts of them. Is that, however, the case?

No! I am sorry to say; for while thirteen distinct lines are recorded, there is not the slightest indication as to their being of any but equal visibility; yet one of them is an actual Sirius for brilliance, the very brightest of all the 1st-magnitude lines or stars, and others are as faint as 15th- and 20th-magnitude stars, seldom seen by any one. Yet of all that he *has* actually seen, I doubt not that Dr. Watts's measured wave-length places are always respectable for accuracy, though not perfect; and I can quite enter into his statement that the best-determined of them all are the lines 5165.5 and 5585.5.

Why or how that result came about is not explained by him; I will therefore proffer two reasons of my own, which will not decrease the interest or importance of the measures.

(1) The line 5165.5 is the first of the green band, the brightest line of the whole carbohydrogen-spectrum, the one which should have been decorated with an  $\alpha$ ; and it was much enlarged on, no less than nineteen years ago, by Professor Swan for its extreme beauty, its brilliance, its definition, and its capacity for being accurately measured. And

(2) The line 5585.5, not the first, but, strange to say, the second of the citron band, was found in 1870 by Piazz Smyth to be so almost exactly coincident with the chief, the almost only, the Angström-discovered aurora-line, that he has recommended it repeatedly since then to all aurora-observers as affording a ready and instantaneous eye-proof whether there is any variety of spectroscopic character in the chief part of the light of successive auroras—he, too, having found none in nearly thirty auroras spread through two or three years, and embracing the widest external variations from arcs of bland light to needle-shaped shooting rays, and from pale yellow-green or citron-



colour up to almost any variety of red\*. During the present year, indeed, Piazzì Smyth has been informed by Mr. Rand Capron, of Guildford, Surrey, that the coincidence is never quite perfect, the aurora-line being slightly *more* refrangible than the second line of the citron band; and Piazzì Smyth is quite ready to bow before this correction from the superior spectroscope with much larger dispersion, and the evident practical ability of Mr. Capron. But the correction still leaves the reference-use of the line 5585·5, though the second of the band (which gradually goes off into invisibility), more important than the first—and just as accurate as before, if each observer will remember that a normal aurora-line reads on the comb-like natural scale of the citron band of the carbohydrogen-spectrum not 2·0, but 2·2—the wave-lengths of all the lines in that interesting band reading thus, according to various authorities:—

BAND of carbo- hydrogen- spectrum.	Lines.		Wave-length according to				
	Numbered from less- refrangible side.	Compara- tive bright- ness as with star magni- tudes.	Swan, Ångström, Lielegg, &c. collected by Piazzì Smyth in 1870.	Swan, in 1871, by projection of his an- gular mea- sures of 1856.	Swan, in 1871, by calculation of the same.	Dr. Watts, in his 'Index of Spectra,' in 1872.	Dr. Watts, in his paper in the Philo- sophical Magazine for Novem- ber 1874.
Citron {	1	1	5630	5630	5629·8	5622	5634·7
	2	1	5579	5570	5576·7	5582	5585·5
	3	3	5535	5525	5532·9	5534	5542·3
	4	6	5497	5488	5495·1	5495	5503·5
	5	10	5460	.....	.....	5463	5478·4

See also Plate II.

How, therefore, Dr. Watts came in 1874 to single out the *second* line of the citron band for super-accurate measurement of place by mere chance, and without knowing any thing more than appears in his paper of my having used it for years as a standard reference for an almost exactly coincident cosmical phenomenon in the night sky, is a strange problem. But its due investigation I must leave untouched on now, as there are other and more world-wide important matters to be discussed in the Doctor's last paragraph, where he states with no little positiveness both what the visible spectrum concerned is chemically the spectrum of, and of what it is not.

\* When the red colour is decided to the eye, a red line appears in the spectrum with wave-length 6290 nearly; but the 5585 citron-line is still always in its due place, and always brighter than the red line, even in the very reddest parts of the aurora.

*Chemical Parentage of the Spectrum under discussion.*

That spectrum is, says Dr. Watts, the spectrum of carbon, and not of a hydrocarbon or any other compound of carbon.

This is so far very plain and distinct as an assertion, and indicates that the learned world of London, as represented by the Philosophical Magazine, is not yet advanced beyond the position it was in when I sent my first paper to the Royal Astronomical Society in May 1871, and gave then such extracts from the authorities on either side as showed, I verily thought, that the spectroscopists declaring for pure carbon, in opposition to those pronouncing for carbohydrogen, were blundering little less than the perpetual-motion men of last century.

For why? Carbon is a simple element in chemistry; and to give its spectrum at all as a luminous and discontinuous one, it must be driven off in vapour, glowing and incandescent.

This is the condition for any and every chemical element to give forth its spectrum under the prism; and some elements will send out their vapour easily enough at very moderate temperatures in any common candle-flame, while others require much more intense heat; for even in a powerful blowpipe-flame they only become hot and luminous as solid bodies, without rendering out any vapour, until the aid of oxygen or the electric spark is brought in. But carbon! why, that has never been volatilized yet by any contrivance or accumulation of contrivances by modern men; so that M. Lielegg in Austria, and Mr. Crookes in the 'Chemical Journal' in England, pronounced years ago that the merely talked-about vapour of carbon was only an hypothesis, a delusion. I have, too, myself seen the full power of a 12-horse steam-engine converted by Mr. Wylde of Manchester into electric currents, and the whole directed for several minutes through a little thin pencil of carbon in a manner that would have melted and dissipated the same bulk of platinum over and over again, but with no other effect than merely to make the carbon, as a solid, white-hot, or just as I have found chloride of magnesium to go on glowing as a hot solid but nothing more (unless to show faintly the lines of *calcium* and *sodium* impurities) in an ordinary blowpipe-flame.

Hence, then, if man has never volatilized carbon, human eye has never yet knowingly seen its spectrum, and can form no idea from theory of what it will be like, except that it will be totally different in kind and species from the many-banded spectrum of ranks of closely arranged perspectives of lines which has been so positively mistaken for it by certain parties. For as Mr. Norman Lockyer has recently shown, that kind of spectrum indicates at once a chemical *compound* of two or more

elements in actual chemical combination ; while, whenever the heat is raised high enough to dissociate those elements, then immediately their several spectra appear as elements ; and *they* give spectra of fine lines only, sharp, well defined, usually far apart, and not affecting in any degree to occupy the place of the bands of the compound.

How, then, came so egregious an error to grow up in the modern world, as to mistake so very unlikely a spectrum and of the most easily volatilized compound, and at the very beginning, instead of end, of its burning, for the most refractory of all the elements ?

The history of errors is always instructive ; and the following seems to have been its course in this carbon case.

*The Rise of the Myth of Carbon-vapour.*

The Royal Society (acting unhappily through its secret committees) first patronized the mistake, by publishing in their Philosophical Transactions Mr. Atfield's paper of 1862, p. 221, wherein he examined, rather cavalierly\*, what Professor Swan

\* As one example :—"The yellow-green (citron) band, composed," says Mr. Atfield (p. 222), "according to the drawing accompanying Swan's paper, of four lines, I find to contain six ; the green band to have five instead of two."

From this statement any one might be led to conclude that there was a definite number of lines of equal observing importance in each band, that Professor Swan had committed a grave error in alluding to only four and two when there were really six and five, and that the new lines might be in spectrum-place either before, behind, or amongst Swan's lines in order of dispersion—entirely therefore destroying the value of his observed spectrum-places of those lines reckoned as first, second, third, &c. of each band, counting from the less-refrangible side.

Yet, in place of this, the new lines only tack on to the fainter and more-refrangible end of a vanishing series, of which Professor Swan correctly described all the components, from the first and brightest up to the last and faintest one *certainly visible in his apparatus*. Mr. Atfield, by an unlimited use of oxygen in place of common air, was able, in a rich London laboratory, to produce more brilliance in the light operated on by his spectroscope, and therefore could carry on the vanishing series, as might well have been expected, a little further ; and since then M. Morren, in Paris, has carried it on further still. But all these additional lines are hardly equal even in collective light and importance to the last line of the series previous to them ; nor do they alter the place of the brighter preceding lines in any degree, either as being the first, second, &c. of each band, or in their recorded wave-lengths.

It is also worthy of note, that there is neither a plate-view, nor a single measured-scale place of any one spectrum-line throughout the whole of Mr. Atfield's paper—an omission of all that is accurate in spectroscopy, of all that has tended to make it a high science, which can only be explained (in a memoir *crowned* by being printed in the Philosophical Transactions of the Royal Society of London) by its one chief burden (viz. putting pure carbon vapour for hydrocarbon) having been grateful to the then already formed prejudices of the secret committee who passed it.

had previously called the carbohydrogen-spectrum, and declared it to be the spectrum of the glowing and incandescent vapour of carbon; wherefore the earlier announced truth of the Scottish professor was extinguished, and the error of the Royal Society became so fashionable in London circles, that every one began to talk thenceforth of that particular spectrum as the undoubted spectrum of "carbon."

Hence, too, when so admirable an observer and inimitable a spectroscopist as Dr. Huggins found the spectra of two small comets resolvable into bands somewhat similar to those of the carbohydrogen, he boldly called them the bands of the carbon-spectrum; and it was approved by the secret committee of the Royal Society and printed in their *Philosophical Transactions* in 1868.

But Dr. Huggins, as a good practical experimenter as well as astronomical observer, knew full well the impossibility of the spectrum of carbon being seen without an almost supernatural degree of heat being applied to it; how, therefore, did he show that such heat existed in the ultra-faint comets which he had spectroscoped?

The method is worthy of the gravest note, as showing (from its being actually printed with honour in the *Philosophical Transactions*) what equivocal conclusions will pass the secret committees of the Royal Society when they correspond with the prejudices of some person or persons behind the scenes there; though those unknown powers do occasionally act as very dragons in keeping out any salutary doubt expressed on a *favoured* topic. For this was the heat-agency announced, viz.:—

That "some comets have approached the sun sufficiently near to acquire a temperature high enough to convert even carbon into vapour."

Not the comets, be it remarked, that were actually the subject of these observations, but some other comets of a totally different form of orbit and infinitely nearer approach to the sun.

Of such totally different comets, too, the only one that was mentioned is the unprecedented comet of 1843, which approached the sun's surface within a distance of a seventh part of the solar radius. But even there, no proof is attempted or demonstration given either of what spectrum that comet would have shown if any one had spectroscoped it (for no one did), or that its temperature *was* high enough to volatilize carbon efficiently for the spectro-scope—only that Sir John Herschel had said that the heat the comet had experienced must have been 47,000 times as intense as what the earth receives from the sun. But as that still more eminent authority in solar spectroscopy, Professor Ångström, has declared since then for there not being heat enough even in

the sun itself to volatilize carbon—why, even if the small comets said, in the Philosophical Transactions, to be throwing off the incandescent vapour of carbon every night they were under observation, even in a dark and cold sky, had been taken thence and placed on the very surface of the sun itself, and had experienced there not only the heat which that other comet had experienced of earth's  $\times 47,000$ , but earth's  $\times 300,000$ , they could not have shown a pure carbon-spectrum.

As our sun, according to Father Secchi, ranks only among the yellow stars, and *they* are supposed not to be so hot as the white stars, perhaps the vapour of carbon may exist glowing and incandescent in Sirius, which is so noted a member of the latter class of stars. We may, too, perhaps be privileged to see the actual and real spectral lines of carbon there, in any good telescope—but with the drawback that, however plainly the lines may appear in themselves, we cannot recognize their chemical origin and assign them their true name, because neither has man ever yet volatilized pure carbon, nor has any angel (in default of theory) ever told us the wave-lengths of carbon-lines when the carbon has been volatilized by a higher power.

Hydrocarbon compound it is given to man to volatilize and spectroscopize; and he should be thankful for its many admirable uses; but as to the spectrum of the pure carbon element being seen in the base of the flame of every little candle made and set alight by human hands, it would be well if certain modern men, and the secret committee of the Royal Society in particular, were to come forward openly and confess with deep contrition in the words of ancient Job,

“I have uttered that I understood not; things too wonderful for me, which I knew not.”

“Wherefore I abhor myself, and repent in dust and ashes.”

#### IV. *Statistics by Intercomparison, with Remarks on the Law of Frequency of Error.* By FRANCIS GALTON, F.R.S.\*

**M**Y object is to describe a method for obtaining simple statistical results which has the merit of being applicable to a multitude of objects lying outside the present limits of statistical inquiry, and which, I believe, may prove of service in various branches of anthropological research. It has already been proposed (Lecture, Royal Institution, Friday evening, February 27, 1874), and in some degree acted upon (*‘Hereditary Genius,’* p. 26), by myself. What I have now to offer is a more complete explanation and a considerable development of previous views.

\* Communicated by the Author.

The process of obtaining mean values &c. now consists in measuring each individual with a standard that bears a scale of equal divisions, and afterwards in performing certain arithmetical operations upon the mass of figures derived from these numerous measurements. I wish to point out that, in order to procure a specimen having, in one sense, the mean value of the quality we are investigating, we do not require any one of the appliances just mentioned: that is, we do not require (1) independent measurements, nor (2) arithmetical operations; we are (3) able to dispense with standards of reference, in the common acceptance of the phrase, being able to create and afterwards indirectly to define them; and (4) it will be explained how a rough division of our standard into a scale of degrees may not unfrequently be effected. Therefore it is theoretically possible, in a great degree, to replace the ordinary process of obtaining statistics by another, much simpler in conception, more convenient in certain cases, and of incomparably wider applicability.

Nothing more is required for the due performance of this process than to be able to say which of two objects, placed side by side, or known by description, has the larger share of the quality we are dealing with. Whenever we possess this power of discrimination, it is clear that we can marshal a group of objects in the order in which they severally possess that quality. For example, if we are inquiring into the statistics of height, we can marshal a number of men in the order of their several heights. This I suppose to be effected wholly by *intercomparison*, without the aid of any external standard. The object then found to occupy the middle position of the series must possess the quality in such a degree that the number of objects in the series that have more of it is equal to that of those that have less of it. In other words, it represents the *mean* value of the series in at least one of the many senses in which that term may be used. Recurring to the previous illustration, in order to learn the mean height of the men, we have only to select the middlemost one and measure him; or if no standard of feet and inches is obtainable, we must describe his height with reference to numerous familiar objects, so as to preserve for ourselves and to convey to strangers as just an idea of it as we can. Similarly the mean speed of a number of horses would be that of the horse which was middlemost in the running.

If we proceed a step further and desire to compare the mean height of two populations, we have simply to compare the representative man contributed by each of them. Similarly, if we wish to compare the performances of boys in corresponding classes of different schools, we need only compare together the middle boys in each of those classes.

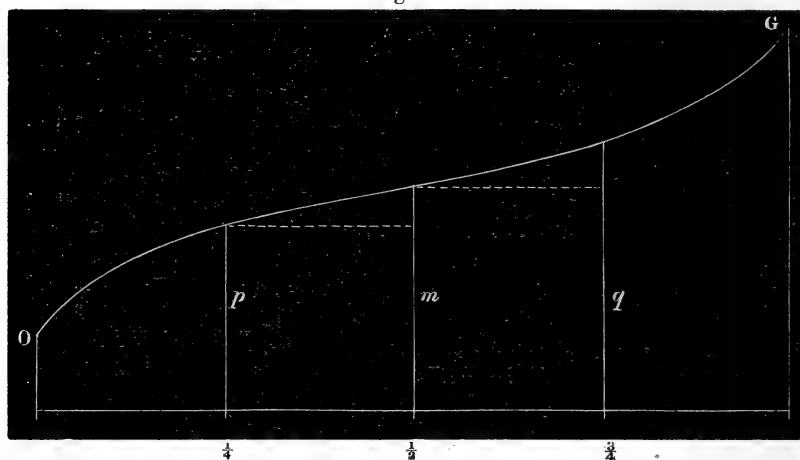
The next great point to be determined is the divergency of the series—that is, the tendency of individual objects in it to diverge from the mean value of all of them. The most convenient measure of divergency is to take the object that has the mean value, on the one hand, and those objects, on the other, whose divergence in either direction is such that one half of the objects in the series on the same side of the mean diverge more than it does, and the other half less. The difference between the mean and either of these objects is the measure in question, technically and rather absurdly called the “probable error.” Statisticians find this by an arithmetical treatment of their numerous measurements; I propose simply to take the objects that occupy respectively the first and third quarter points of the series. I prefer, on principle, to reckon the divergencies in excess separately from those in deficiency. They cannot be the same unless the series is symmetrical, which experience shows me to be very rarely the case. It will be observed that my process fails in giving the difference (probable error) in numerical terms; what it does is to select specimens whose differences are precisely those we seek, and which we must appreciate as we best can.

We have seen how the mean heights &c. of two populations may be compared; in exactly the same way may we compare the divergencies in two populations whose mean height is the same, by collating representative men taken respectively from the first and third quarter points of the series in each case.

We may be confident that if any group be selected with the ordinary precautions well known to statisticians, it will be so far what may be called “generic” that the individual differences of members of that group will be due to various combinations of pretty much the same set of variable influences. Consequently, by the well-known laws of combinations, medium values will occur very much more frequently than extreme ones, the rarity of the latter rapidly increasing as the deviation slowly increases. Therefore, when the objects are marshalled in the order of their magnitude along a level base at equal distances apart, a line drawn freely through the tops of the ordinates which represent their several magnitudes will form a curve of double curvature. It will be nearly horizontal over a long space in the middle, if the objects are very numerous; it will bend down at one end until it is nearly vertical, and it will rise up at the other end until there also it is nearly vertical. Such a curve is called, in the phraseology of architects, an “ogive,” and is represented by O G in the diagram (fig. 1), in which the process of statistics by intercomparison is clearly shown. If  $n$  = the length of the base of the ogive, whose ordinate  $y$  represents the magni-

tude of the object that stands at a distance  $x$  from that end of the base where the ordinates are smallest, then the number of

Fig. 1.



objects less than  $y$ : the number of objects greater than  $y :: x : n - x$ . The ordinate  $m$  at  $\frac{1}{2}$  represents the mean value of the series, and  $p, q$  at  $\frac{1}{4}$  and  $\frac{3}{4}$ , taken in connexion with  $m$ , give data for estimating the divergence; thus  $q - m$  is the divergence (probable error) of at least that portion of the series that is in excess of the mean, and  $m - p$  is that of at least the other portion. When the series is symmetrical,  $q - m = p - m$ , and either, or the mean of both, may be taken as the divergence of the series generally. No doubt we are liable to deal with cases in which there may be some interruption in the steady sweep of the ogive; but the experience of qualities which we *can* measure, assures us that we need fear no large irregularity of that kind when dealing with those which, as yet, we have no certain means of measuring.

When we marshal a series, we may arrange them roughly, except in the neighbourhood of the critical points; and thus much labour will be saved. But the most practical way of setting to work would probably depend not on the mere discrimination of greater and less, but also on a rough sense of what is much greater or much less. We have called the objects at the  $\frac{1}{4}$ ,  $\frac{1}{2}$ , and  $\frac{3}{4}$  distances  $p, m$ , and  $q$  respectively; let us sort the objects into two equal portions P and Q, of small and great, taking no more pains about the sorting than will ensure that P contains  $p$  and all smaller than  $p$ , and that Q contains  $q$  and all larger than  $q$ . Next, beginning, say, with group P, sort away alternately to right and left the larger and the smaller objects,



roughly at first, but proceeding with more care as the residuum diminishes and the differences become less obvious. The last remaining object will be  $p$ . Similarly we find  $q$ . Then  $m$  will be found in the same way from the group compounded of those that were sorted to the right from  $P$  and to the left from  $Q$ .

There are not a few cases where both the ordinary method and that by intercomparison are equally applicable, but in which the latter would prove the more rapid and convenient. I would mention one of some importance to those anthropologists who may hereafter collect data in uncivilized countries. A barbarian chief might often be induced to marshal his men in the order of their heights, or in that of the popular estimate of their skill in any capacity; but it would require some apparatus and a great deal of time to measure each man separately, even supposing it possible to overcome the usually strong repugnance of uncivilized people to any such proceeding.

The practice of sorting objects into classes may be said to be coextensive with commerce, the industries, and the arts. It is adopted in the numerous examinations, whether pass or competitive, some or other of which all youths have now to undergo. It is adopted with every thing that has a money-value; and all acts of morality and of intellectual effort have to submit to a verdict of "good," "indifferent," or "bad."

The specimen values obtained by the process I have described are capable of being reproduced so long as the statistical conditions remain unchanged. They are also capable of being described in various ways, and therefore of forming permanent standards of reference. Their importance then becomes of the same kind as that which the melting-points of well-defined alloys or those of iron and of other metals had to chemists when no reliable thermometer existed for high temperatures. These were excellent for reference, though their relations *inter se* were subject to doubt. But we need never remain wholly in the dark as to the relative value of our specimens, methods appropriate to each case being sure to exist by which we may gain enlightenment. The measurement of work done by any faculty when trained and exerted to its uttermost, would be frequently available as a test of its absolute efficacy.

There is another method, which I have already advocated and adopted, for gaining an insight into the absolute efficacies of qualities, on which there remains more to say. Whenever we have grounds for believing the law of frequency of error to apply, we may *work backwards*, and, from the relative frequency of occurrence of various magnitudes, derive a knowledge of the true relative values of those magnitudes, expressed in units of probable error. The law of frequency of error says that "mag-

nitudes differing from the mean value by such and such multiples of the probable error, will occur with such and such degrees of frequency." My proposal is to reverse the process, and to say, "since such and such magnitudes occur with such and such degrees of frequency, therefore the differences between them and the mean value are so and so, as expressed in units of probable error." According to this process, the positions of the first divisions of the scale of divergence, which are those of the mean value *plus* or *minus* one unit of probable error, are of course  $p$  and  $q$ , lying at the  $\frac{1}{4}$  and  $\frac{3}{4}$  points of the ogive, or, if the base consist of 1000 units, at the 250th point from the appropriate end. The second divisions being those of mean value *plus* or *minus* two units of probable error, will, according to the usual Tables, be found at the 82nd point from the appropriate end, the third divisions will be at the 17th, and the fourth at the 3rd. If we wished to pursue the scale further, we should require a base long enough to include very many more than 1000 units.

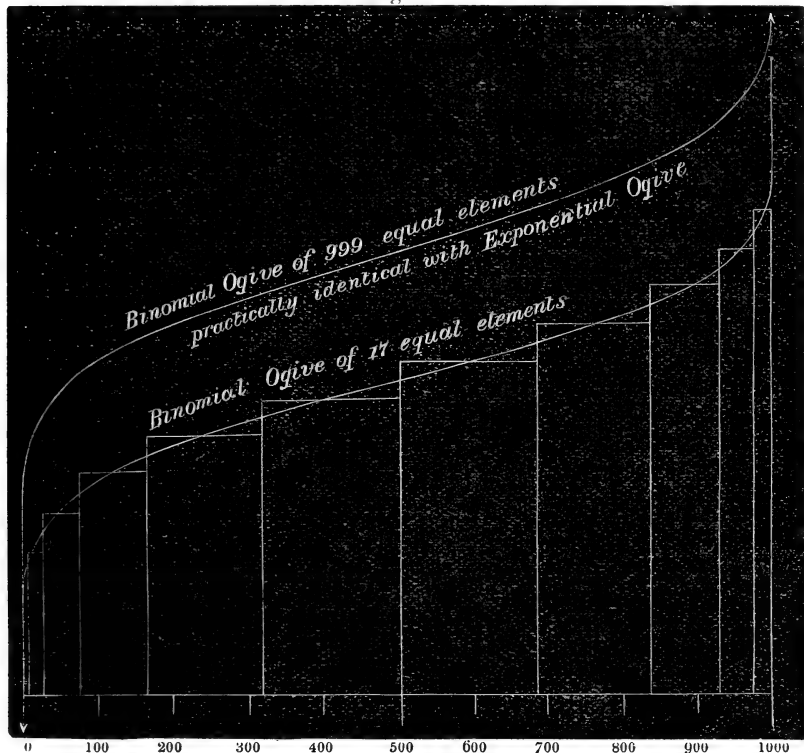
#### *Remarks on the Law of Frequency of Error.*

Considering the importance of the results which admit of being derived whenever the law of frequency of error can be shown to apply, I will give some reasons why its applicability is more general than might have been expected from the highly artificial hypotheses upon which the law is based. It will be remembered that these are to the effect that individual errors of observation, or individual differences in objects belonging to the same generic group, are entirely due to the aggregate action of variable influences in different combinations, and that these influences must be (1) all independent in their effects, (2) all equal, (3) all admitting of being treated as simple alternatives "above average" or "below average;" and (4) the usual Tables are calculated on the further supposition that the variable influences are infinitely numerous.

As I shall lay much stress on matters connected with the last condition, it will save reiteration if I be permitted the use of a phrase to distinguish between calculations based on the supposition of a moderate number ( $r$ ) of elements (in which case the frequency of error or the divergence is expressed by the coefficients of the expansion of the binomial  $(a+b)^r$ ) and one based on the supposition of the number being infinite (which is expressed by the exponential  $e^{-\frac{x^2}{c^2}}$ ), by calling the one the binomial and the other the exponential process, the latter being the process to be understood whenever the "law of frequency of error" is spoken of without further qualification. When the results of

these two processes have to be protracted, as in figure 2, the unit of vertical measurement in the case of a series of bino-

Fig. 2.



mial grades will be a single grade, or, what comes to the same thing, the difference of the effect produced by the plus and minus phase of any one of the alternative elements, upon the value of the whole. The unit of the exponential curve will be  $q-m$  of fig. 1, or the probable error. This latter unit is equally applicable to what we may call the binomial ogive, which is the curve drawn with a free hand through the grades. The justification for such a conception as a binomial ogive will be fully established further on. Suffice it for the present to remark that, by the adoption of a unit of this kind, the middle portion of a binomial ogive of 999 elements is compared in the figure with one of 17.

The first three of the above-mentioned conditions may occur in games of chance, but they assuredly do not occur in vital and social phenomena ; nevertheless it has been found in numerous

instances, where measurement was possible, that the latter conform very fairly, within the limits of ordinary statistical inquiry, to calculations based on the (exponential) law of frequency of error. It is a curious fact, which I shall endeavour to explain, that in this case a false hypothesis, which is undoubtedly a very convenient one to work upon, yields true results.

In illustration of what occurs in nature, let us consider the causes which determine the size of fruit. Some are important, the chief of which is the Aspect, whose range of influence is too wide to permit us to consider it in one of the simple alternatives "good" or "bad." It is no satisfactory argument to say that variations in aspect are *partly* due to a multitude of petty causes, such as the interposition of leaves and boughs, because, so far as they depend on well-known functions of altitude and azimuth, they cannot be reduced to a multitude of elementary causes. There has been much confusion of ideas on this subject, and also a forgetfulness of another fact—namely, that when we once arrive at a simple alternative, there our subdivision of causes must stop, and we must accept that alternative, however great may be its influence, as one of the primary elements in our calculation.

In addition to important elements, there are others of small, but still of a recognizable value, such as exposure to prevalent winds, the pedigree of the tree, the particular quality of the soil on which it stands, the accident of drains running near to its root, &c. Again, there are a multitude of smaller influences, to the second, third, and fourth orders of minuteness.

I shall proceed to define what I mean by "small;" then I shall show how this medley of causes may admit of being theoretically sorted into a moderate number of small influences of equal value, giving a first approximation to the truth; then how, by a second approximation, the grades of the binomial expansion thence derived become smoothed into a flowing curve. Lastly, I shall show by quite a different line of argument that the exponential view contains inherent contradictions when nature is appealed to, that the binomial of a moderate power is the truer one, and that we have means of ascertaining a limit which the number of its elements cannot exceed. My conclusion, so far as this source of difficulty is concerned, is that the exponential law applies because it nearly resembles the curve based on a binomial of moderate power, within the limits between which comparisons are usually made.

We observe in fig. 2 how closely the outline of an exponential ogive resembles that of a binomial of a very moderate number of elements, within the narrow limits chiefly used by statisticians. The figure expresses a series of 1000 objects marshalled accord-

ing to their magnitudes. In the one case the magnitudes are supposed to be wholly due to the various combinations of 17 alternatives, and the elements of the drawing are obtained from the several terms of the expansion of  $(1+1)^{17}$ , all multiplied into  $\frac{1000}{2^{17}}$ . These form the following series, reckoning to the nearest integer; and their sum, of course, = 1000:—0, 0, 1, 5, 18, 47, 95, 148, 186, 186, 148, 95, 47, 18, 5, 1, 0, 0. In the figure these proportions are protracted so far as possible; but the numbers even in the fourth grade are barely capable of being represented on its small scale; after the fourth, the several grades are manifest until we reach the corresponding point at the opposite end of the series. Then, with a free hand, a curve is drawn through them, which gives as their mean value 8.5, as it ought to do. Now, referring to our  $p$  and  $q$  at the 250th division from either end, I measure the value of  $q-m$  (or  $m-p$ ), which is the unit to which I must reduce any other ogive that I may desire to compare with the present one. Also I can find the values for  $m+2(q-m)$  and  $m+3(q-m)$ , which is going as far as a figure on this small scale admits. I now protract the central portion of an exponential ogive to the same scale, horizontally and vertically. Not knowing its base, I start from its middle point, placing it arbitrarily at a convenient position in the prolongation of the  $m$  of the binomial; and I lay off, in the prolongation of  $p$  and  $q$ , points that are respectively 1 unit of probable error less and greater than  $m$ . The Tables of the law of error tell me where to lay off the other points; and so the curve is determined. It must be clearly understood that whereas in the figure both the ogive and the base are given for the binomial series of 17 elements, it is only the ogive that is given for the exponential, there being no data to determine the position of its base. The comparison is simply between the middle portions of the ogives. To speak correctly, I have not actually used the exponential Tables to draw the exponential curve, but have used Quetelet's expansion of a binomial of 999 elements, the results of which are identical, as he has shown, with those of the exponential to within extremely minute fractions, utterly insensible in a scale more than a hundred times as great as the present one.

I find the position of the various points in the two ogives, measured from the appropriate end of the base, to be as is expressed in the following Table:—

	In binomial ogive of 17 elements.	In exponential ogive, or in binomial ogive of 999 elements.
The mean .....	500	500
The mean $\pm 1$ unit probable error ...	250	250
„ $\pm 2$ units .....	71	82
„ $\pm 3$ units .....	16	17

The closeness of the resemblance is striking. It rapidly increases and extends in its range as the number of elements in the binomial increases; there need therefore be no hesitation in recognizing the fact that a binomial of, say, 30 elements or upwards is just as conformable to ordinary statistical observation as is the exponential. If one agrees, the other does, because they agree with one another.

The fewest number of elements that suffice to form a binomial having the above-mentioned conformity is a criterion of the meaning of the word “small,” which was lately employed, because each of those elements would be just entitled to rank as small.

I obtain the value of any one of them in an ogive by protracting the series and noticing how many grades are included in the interval  $q-m$ . It will be found that in a binomial of 17 elements  $q-m$  is equal to eight fifths of one grade. Thence I conclude that in any generic series an influence the range of whose mean effects in the two alternatives of above and below average is not greater than, say, one half of the probable error of the series, is entitled to be considered “small.”

I now proceed to show how a medley of small and minute causes may, as a first approximation to the truth, be looked upon as an aggregate of a moderate number of “small” and *equal* influences. In doing this, we may accept without hesitation, the usual assumption that all small, and *à fortiori* all minute influences, may be dealt with as simple alternatives of excess or deficiency—the values of this excess and deficiency being the mean of all the values in each of these two phases. The way in which I propose to build up the fictitious groups may be exactly illustrated by a game of odd and even, in which it might be agreed that the *predominance* of “heads” in a throw of three fourpenny pieces, shall count the same as the simple “head” of a shilling. The three fourpenny pieces may fall all heads, 2 heads and 1 tail, 1 head and 2 tails, or all tails—the relative frequency of these events being, as is well known, 1, 3, 3, 1. But by our hypothesis we need not concern ourselves about these minute peculiarities; the question for us is simply the alternative one, are the “heads” in a majority or not? We may therefore treat a ternary system of the third order of smallness exactly as a simple alternative of the first order of smallness. Or, again,

suppose a crown were our "small" unit, and we had a medley of 10 crowns, 33 shillings, and 100 fourpenny pieces, with which to make successive throws, throwing the whole number of them at once: we might theoretically sort them into fictitious groups each equivalent to a crown. There would be 29 such groups, viz.:—10 groups, each consisting of 1 crown; 6 groups, each of 5 shillings; 1 group of three shillings and 6 fourpenny pieces; 6 groups each of 15 fourpenny pieces; and a residue of 4 fourpenny pieces, which may be disregarded. Hence, on the already expressed understanding that we do not care to trouble ourselves about smaller sums than a crown, the results of the successive throws of the medley of coins would be approximately the same as those of throwing at a time 29 crowns, and would be expressed by the coefficients of a binomial of the 29th power. Hence I conclude that all miscellaneous influences of a few small and many minute kinds, may be treated for a first approximation exactly as if they consisted of a moderate number of small and equal alternatives.

The second approximation has already been alluded to; it consists in taking some account of the minute influences which we had previously agreed to ignore entirely, the effect of which is to turn the binomial grades into a binomial ogive. I effect it by drawing a curve with a free hand through the grades, which affords a better approximation to the truth than any other that can *à priori* be suggested.

I will now show from quite another point of view (1) that the exponential ogive is, on the face of it, fallacious in a vast number of cases, and (2) that we may learn what is the greatest possible number of elements in the binomial whose ogive most nearly represents the generic series we may be considering. The

value of  $\frac{m}{q-m}$  is directly dependent on the number of elements; hence, by knowing its value, we ought to be able to determine the number of its elements. I have calculated it for binomials of various powers, protracting and interpolating, and obtain the following very rough but sufficient results for their ogives (not grades):—

Number of (equal) elements.	Value of $\frac{m}{q-m}$ .
17 . . . . .	5
32 . . . . .	10
65 . . . . .	15
107 . . . . .	20
145 . . . . .	25
186 . . . . .	30
999 . . . . .	48

Now, if we apply these results to observed facts, we shall rarely find that the series has been due to any large number of equal elements. Thus, in the stature of man the probable error,

$\frac{m}{q-m}$ , is about 30, which makes it impossible that it can be looked upon as due to the effect of more than 200 equally small elements. On consideration, however, it will appear that in certain cases the number may be *less*, even considerably less, than the tabular value, though it can never exceed it. As an illustration of the principle upon which this conclusion depends,

we may consider what the value of  $\frac{m}{q-m}$  would be in the case

of a wall built of 17 courses of stone, each stone being 3 inches thick, and subject to a mean error in excess or deficiency of one fifth of an inch. Obviously the mean height  $m$  of the wall would be  $3 \times 17$  inches; and its probable error  $q-m$  would be very small, being derived from a binomial ogive of 17 elements, each of the value of only one fifth of an inch. Now we saw from our previous calculation that this would be eight fifths, or 1.6 inch, which would give the value to  $\frac{m}{q-m}$  of  $\frac{51}{1.6}$ , or about 321;

consequently we should be greatly misled if, after finding by observation the value of that fraction, and turning to the Table and seeing there that it corresponded to more than 200 equal elements, we should conclude that that was the number of courses of stones. The Table can only be trusted to say that the number of courses certainly does not exceed that number; but it may be less than that.

The difficulty we have next to consider is that which I first mentioned, but have intentionally postponed. It is due to the presence of influences of extraordinary magnitude, as Aspect in the size of fruit. These influences must be divided into more than two phases, each differing by the same constant amount from the next one, and that difference must not be greater than exists between the opposite phases of the "small" alternatives. If we had to divide an influence into three phases, we should call them "large," "moderate," and "small;" if into four, they would be "very large," "moderately large," "moderately small," and "very small," and so on. Any objects (say, fruit) which are liable to an influence so large as to make it necessary to divide it into three phases, really consist of three series generically different which are entangled together, and ought theoretically to be separated. If there had been two influences of three phases, there would be nine such series, and so on. In short, the fruit, of which we may be considering some hundred or a few thousand



specimens, ought to be looked upon as a multitude of different sorts mixed together. The proportions *inter se* of the different sorts may be accepted as constant; there is no difficulty arising from that cause. The question is, why a mixture of series radically different, should in numerous cases give results apparently identical with those of a simple series.

For simplicity's sake, let us begin with considering only one large influence, such as aspect on the size of fruit. Its extreme effect on their growth is shown by the difference in what is grown on the north and south sides of a garden-wall, which in such kinds of fruit as are produced by orchard-trees, is hardly deserving of being divided into more than three phases, "large," "moderate," and "small." Now if it so happens that the "moderate" phase occurs approximately *twice as often* as either of the extreme phases (which is an exceedingly reasonable supposition, taking into account the combined effects of azimuth, altitude, and the minor influences relating to shade from leaves &c.), then the effect of aspect will work in with the rest, just like a binomial of two elements. Generally the coefficients of  $(a+b)^n$  are the same as those of  $(a+b)^{n-r} \times (a+b)^r$ . Now the latter factor may be replaced by any variable function the frequency and number of whose successive phases, into which it is necessary to divide it, happen to correspond with the value of the coefficients of that factor.

It will be understood from what went before, that we are in a position to bring these phases to a common measure with the rest, by the process of fictitious grouping with appropriate doses of minute influences, as already described.

On considering the influences on which such vital phenomena depend as are liable to be treated together statistically, we shall find that their mean values very commonly occur with greater frequency than their extreme ones; and it is to this cause that I ascribe the fact of large influences frequently working in together with a number of small ones without betraying their presence by any sensible disturbance of the series.

The last difficulty I shall consider, arises from the fact that the individuals which compose a statistical group are rarely affected by exactly the same number of variable influences. For this cause they ought to have been sorted into separate series. But when, as is usually the case, the various intruding series are weak in numbers, and when the number of variable influences on which they depend does not differ much from that of the main series, their effect is almost insensible. I have tried how the figures would run in many supposititious cases; here is one taken at haphazard, in which I compare an ordinary series due to 10 alternatives, giving  $2^{10} = 1024$  events, with a compound series.

The latter also comprises 1024 events; but it is made up of three parts: viz. nine tenths of it are due to a 10-element series; and of the remaining tenth, half are due to a 9 and half to an 11 series. I have reduced all these to the proper ratios, ignoring fractions. It will be observed how close is the correspondence between the compound and the simple series.

Total cases.	Number of elements.	Successive grades in the series.											
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
52	9	0	1	4	8	13	13	8	4	1	0	0	0
924	10	1	9	41	108	189	227	189	108	41	9	1	0
48	11	0	0	1	4	8	11	11	8	4	1	0	0
1024	Compound series.	1	10	46	120	210	251	208	120	46	10	1	0
1024	10	1	10	45	120	210	252	210	120	45	10	1	0
	Difference .....	0	0	+1	0	0	-1	-2	0	+1	0	0	0

It appears to me, from the consideration of many series, that the want of symmetry commonly observed in the statistics of vital phenomena is mainly due to the inclusion of small series of the above character, formed by alien elements; also that the disproportionate number of extreme cases, as of giants, is due to this cause.

The general conclusion we are justified in drawing appears to be, that, while each statistical series must be judged according to its peculiarities, a law of frequency of error founded on a binomial ogive is much more likely to be approximately true of it than any other that can be specified *à priori*; also that the exponential law is so closely alike in its results to those derived from the binomial ogive, under the circumstances and within the limits between which statisticians are concerned, that it may safely be used as hitherto, its many well-known properties being very convenient in all cases where it is approximately true. Therefore, if we adopt any uniform system (such as already suggested) of denoting the magnitudes of qualities for the measurement of which no scale of equal parts exists, such system may reasonably be based on an *inverse* application of the law of frequency of error, in the way I have described, to statistical series obtained by the process of *intercomparison*.

V. *On a new Method of investigating the Composite Nature of the Electric Discharge.* By ALFRED M. MAYER\*.

IN 1842 Professor Joseph Henry† observed that when a needle was placed in a helix and magnetized by the discharge of a Leyden jar, the direction of the polarity of the needle varied with the "striking-distance" of the jar; and these observations led Henry to the discovery that the discharge was multiple and oscillatory in its nature. In 1862 Feddersen‡ confirmed Henry's discovery, on examining the nature of the discharge by means of a revolving mirror. Subsequently Rood (in a series of classical researches, published in Silliman's *American Journal*, in 1869, 1871, 1872) studied the multiple character of the discharge of the inductorium by means of rotating disks perforated with narrow radial slits. In 1873 Cazin§ also investigated the discharge with the rotating disk. The method I have devised leads us directly, by the simplest means, to phenomena which cannot be revealed by either revolving mirror or rotating disk. The first method that occurred to me was to attach a delicate metallic point to a vibrating tuning-fork, and to send the discharge from this point through lamp-blackened paper to a revolving metallic cylinder on which the paper was stretched. We can to some extent analyze the electric discharge, in these conditions, from the series of perforations left in the paper in the trail of the vibrating fork. This method, though beautiful as an illustration, is useless as a means of investigation; for the metal cylinder, the paper, and the fork form a species of Leyden jar, which is always in the circuit of the particular discharge whose nature you would investigate. The above method, though original with me, cannot be claimed as my own, having recently found that it was devised by Donders||, and has been used in an investigation by Nyland¶. To get rid of inductive action in the registering apparatus, I devised the following method:—A cylinder is covered with thin printing-paper; and the latter is well blackened by rotating the cylinder over burning camphor. The paper is then removed from the cylinder, and cut into disks about 15 centims. in diameter. When one of these disks is re-

\* From Silliman's *American Journal* for December 1874.

† *Proc. Amer. Phil. Soc.*

‡ "Ueber die electrische Flaschenentladung," *Pogg. Ann.* vol. cxvi. p. 132.

§ *Journal de Physique*, vol. ii. p. 252.

|| *Onderzoekingen gedaan in het Physiologisch Laboratorium der Utrechtsche Hoogeschool*, 1868-69.

¶ *Archives Néerlandaises des Sciences exactes et naturelles*, vol. v. p. 292.

volved about twenty times per second, it is rendered very flat by centrifugal action. It can then be brought between points or balls, even when the latter are separated by no more than  $\frac{3}{4}$  millim. When in this position, the discharge between the points or balls perforates the disk and leaves a permanent record of its character, of the duration of the whole discharge, and of the intervals separating its constituent flashes and sparks. To obtain the time of rotation of the disk, I use the method invented by Young in 1807 (see his 'Natural Philosophy,' vol. i. p. 191); that is, I present momentarily to the rotating disk a delicate point which is attached to a vibrating tuning-fork. The number of vibrations per second of this fork has been determined to the last degree of precision by means of a break-circuit clock, which sends at each second a spark from an inductorium through the fork's sinuous trace on blackened paper covering a revolving cylinder. The axis of the sinuous line on the disk is traced with a needle point; and then, on drawing radii through symmetrical intersections of this axis on the sinuous line, we divide the disk off into known fractions of time. The disk is now removed from the rotating apparatus, and the carbon is fixed by floating the disk for a moment on thin spirit-varnish. When the disk is dry and flat it is centred on a divided circle provided with a low-power reading-microscope; and the duration of the whole discharge, and the intervals separating its components, can be determined to the  $\frac{1}{50000}$  of a second.

Many results have been obtained with this apparatus. I defer their publication until I have carefully examined them and have extended this research with the study not only of the discharge of the inductorium, but also of the frictional machine, of the Leyden jar, and of the Holtz machine, under every condition of charged surface and of striking-distance, and when the current is flowing freely over a conductor and when it is doing work. I here present, merely as examples of the value of the method, the results I have obtained in three conditions of experiment.

1. *Discharge of large inductorium\* between platinum points one millim. apart. No jar in the circuit.*

The platinum electrodes were neatly rounded and formed on wire  $\frac{6}{10}$  millim. in diameter. After the discharge through the rotating disk, nothing was visible on it except a short curve formed of minute, thickly set white dots; but on holding the disk between the eye and the light, it was found to be perforated with thirty-three clean round holes with the carbon undis-

\* The striking-distance of this coil between brass points was 45 centims.

turbed around their edges. The portion of the discharge which makes these holes lasts  $\frac{1}{23}$  second; and the holes are separated by intervals which gradually decrease in size toward the end of the discharge, so that the last spark-holes are separated about one half of the distance which separates the holes made at the beginning of the discharge. The *average* interval between the spark-holes is  $\frac{1}{759}$  second. After this portion of the discharge has passed there is a period of quiescence lasting about  $\frac{1}{1500}$  second; then follows a shower of minute sparks, which forms the short dotted line above spoken of. This spark-shower lasts  $\frac{1}{330}$  of a second, and is formed of 30 sparks; hence the average interval separating these sparks is  $\frac{1}{9900}$  second. The intervals separating these sparks, however, are not uniform, but are smaller in the middle of the spark-shower than at the beginning and at the end of this phenomenon. The spark-shower, indeed, is a miniature of the phenomenon obtained when a Leyden jar is placed in the circuit of the coil, and which is described below. The above numbers were determined as the average measures on six disks. It is here to be remarked that all the discharges studied in this paper were made by suddenly depressing the platinum-faced "break" of the primary circuit, and the break was held in this position until the disk had been removed from between the points or balls.

2. *Discharge of large inductorium between platinum points one millim. apart, with a Leyden jar of 242 sq. centims. connected with the terminals of the secondary coil.*

After this discharge through the disk a very remarkable appearance is presented, the full description of which I reserve for a more extended paper. The discharge in its path around the disk dissipates little circles of carbon. There are 91 of these circles, each perforated by 4, 3, 2, or 1 hole. I shall here have to adopt a new nomenclature for the description of this complex phenomenon. I call the whole act of discharge of the coil *the discharge*. Those separate actions which form the little circles by the dissipation of the carbon I denominate *flashes*; and the perforations in these circles I call *sparks*. The discharge in the above experiment lasts  $\frac{1}{24}$  of a second. The flashes at the beginning of the discharge are separated by intervals averaging  $\frac{1}{555}$  second up to about the tenth flash; after this the intervals of the flashes rapidly close up, so that during the fourth fifth of the discharge they follow at each  $\frac{1}{5832}$  of a second. During the last fifth of the discharge the intervals between the flashes gradually increase, and the last flash is separated from its predecessor by  $\frac{1}{1000}$  of a second.

3. *Discharge of large inductorium between brass balls, one centim. in diameter, separated one millim., with a Leyden jar of*  
*Phil. Mag. S. 4. Vol. 49. No. 322. Jan. 1875.* E

242 sq. centims. inner coating, connected with the terminals of the secondary coil.

This discharge also lasts  $\frac{1}{24}$  second, and is similar to the preceding, except that larger circles are made on the disk by the dissipation of the carbon, and that there are fewer flashes, viz. 71. The total number of spark-holes in these flashes is 123. Thus there are fewer flashes than in the experiments with the platinum points, but the total number of spark-holes is the same in each case. Hence there is, on an average, 1.34 spark to each flash with the points, and 1.73 spark-hole to each flash with the balls.

Experiments have also been made with rotating disks formed of "sensitized" paper; and interesting results have been obtained.

## VI. On Polarization by Diffusion of Light.

By J.-L. SORET\*.

### *On the Reflecting-power of Flames.*

**I** PUBLISHED, some months since, a first Note†, on the occasion of a memoir by M. G.-A. Hirn, in which he put forth the hypothesis that the incandescent solid particles which, according to Davy's theory, produce the brightness of flames, become transparent at the high temperature to which they are raised, and no longer possess any sensible reflecting-power. One of the arguments which he advances in support of his hypothesis consists in the fact that no phenomena of polarization are observed in the light of a flame exposed to the rays of the sun.

I indicated the results I had obtained by causing a pencil of solar light to fall on lampblack, either when deposited on another body, or at the moment of its formation—that is to say, when it is in the state of smoke or of a smoky flame. In this latter case the trace of the pencil of solar rays is perfectly visible: the part of the flame which receives the rays appears bluish white, contrasting with the reddish tint of the adjacent parts. If the trace be observed with an analyzer, the light diffused in a direction at right angles to the incident pencil is seen to be completely polarized in the

\* Translated from a separate impression, communicated by the Author, from the *Archives des Sciences* of the *Bibliothèque Universelle*, July 1874, pp. 1-26. An abstract of this memoir has been communicated to the Paris Academy.

† "On some Phenomena of Polarization by Diffusion of Light" (*Archives*, Nov. 18, 1873, vol. xlviii. p. 231), *Phil. Mag.* S. 4. vol. xlvii. p. 205. I take this opportunity to point out two important misprints in that Note (*Archives*, pp. 235, 238): *Phil. Mag. t. c.* p. 208, line 12-13, for horizontal read vertical; p. 209, line 10 from bottom, for 50° read 90°.

plane of vision, so that the white trace ceases to be visible when the analyzer is turned so as to intercept the rays which are polarized in the plane containing the eye and the pencil of solar light.

When the flame is not smoky and when complete combustion augments its brilliance, I had found, like M. Hirn, that the polarization-phenomena are not sensible; but I expressed some doubts of the necessity of concluding from this the absence of the reflecting-power of the particles at a high temperature; the dazzling of the eye and the less quantity of these particles in a brilliant flame, in comparison with a smoky flame, appeared to me sufficient to account for the facts.

I have since endeavoured to control this way of viewing the subject by concentrating the sunlight much more than I had previously done, so as to give more brightness to its trace.

The sunlight, reflected from a silvered mirror, falls upon a good achromatic lens of 72 millims. aperture and 1.5 metre focal length. Lastly, when greater concentration is required, a second lens, much more convergent, is added, near the focus of the first. The flame is then placed at the point where the image of the sun is found.

Working thus with different flames proceeding from carburetted substances, the trace of the sun's rays can be perceived, in most cases, very distinctly, and the usual phenomena of polarization ascertained. When the flame is not too bright, and does not fatigue the eye, the observation is readily made, by aid of a Nicol, with the naked eye; but if the flame is dazzling, there is a great advantage in looking through one or several plates of blue (cobalt) glass. The portions of the flame which do not receive the light of the sun appear then of a purple tint, while the trace of the pencil is clearly distinguished by its blue colour. If observed through the Nicol in the proper position, the blue trace disappears, and the whole flame appears purple.

I have verified these facts in the following cases:—the flame of a wax candle; flame of ordinary gas from a Bengel burner with a glass chimney, or from a butterfly burner; flame of illuminating gas strongly carburetted, butterfly burner; flame of a petroleum lamp, and of a moderator lamp with oil.

I finally tried the very brilliant flame obtained by burning illuminating gas strongly carburetted, with the addition of oxygen. With the process of concentration of the sunlight above described, the trace and its polarization are still distinctly observed as long as the oxygen is not too abundant, the brightness being, however, already incomparably more vivid than that of an ordinary flame.

By employing more energetic means of concentration—that

is to say, by causing the sunlight, reflected by the large mirror of a siderostat, to pass through an objective of 8 inches aperture, and then through a lens of short focus, I could perceive the trace on this flame of carburetted gas fed by a larger proportion of oxygen than in the preceding case; but when the oxygen became too abundant, the trace was no longer visible—which, beside difficulties of observation, may be explained, 1st, by the fact that, the flame having become quite white and even bluish, there is no longer any difference of tint between the part which receives the solar rays and the parts which do not receive them, the trace can only manifest itself by a difference of intensity more difficult to perceive; 2nd, by the carbon particles being immediately consumed at the moment of their formation, and consequently the reflecting matter becoming relatively much rarer.

In short, these experiments show that carbon retains its reflecting-power at very elevated temperatures, which temperatures it would nevertheless be difficult to state precisely.

Further, these facts appear to me to have some interest because they confirm, at least for ordinary flames, the theory of Davy, which has recently been strongly contested; in fact, a pencil of solar light is reflected by diffusion and polarized in precisely the same manner, whether it falls on a very brilliant flame, or whether it illuminates non-incandescent smoke, in which the presence of carbon particles is incontestable.

#### *The Cause of the Illumination of Transparent Bodies and of Diffusion.*

In my former publications I have maintained the opinion that the illumination of transparent bodies traversed by a pencil of rays must be attributed to a defect of homogeneity in the medium—a defect consisting most frequently in the dissemination of foreign particles of great tenuity, but may also result from differences of refrangibility in the component parts of the medium, or, in the case of a solid body, from minute voids or fissures. In other terms, illumination is for me only a particular case of diffusion of light.

My learned friend M. Lallemand attributes this phenomenon to the molecules themselves of the transparent body; he regards the illumination as a lateral propagation of the incident luminous motion, caused by the condensation of the æther around each molecule. Thus, for him, a pencil of light traversing a body which is transparent, not fluorescent, and absolutely homogeneous, must in general give rise to a trace visible laterally, and the phenomenon must depend essentially on the nature itself of the medium in which it is produced.



M. Lallemand, however, in a recent communication relative to what he calls the illumination of opaque bodies with a dead surface\* (that is to say, on diffusion), seems to me to have taken an important step towards my view. In other interesting observations, he has arrived, for a smoked surface, at a result identical with that which I made known in my previous Note, viz. that the light diffused by lampblack is subject, with respect to its polarization, to precisely the same laws as the light emitted by the trace of a pencil of rays traversing a transparent body†.

Now the lampblack covering a slip of glass, for example, is only an agglomeration of very minute particles in juxtaposition. It seems evident that these particles must continue to diffuse the light according to the same laws, but with less intensity, when, instead of being sufficiently abundant to be contiguous and heaped up on one another, they are more scattered and form only a light deposit on the glass, which partially retains its transparency. This is, in fact, confirmed by experiment. No more can this property be refused to the same particles in suspension in a gas (that is, in the state of smoke or flame), or in suspension in a liquid (for instance, water containing a little Indian ink). It must hence be concluded, therefore, that, given a medium destitute by itself of all power of illumination, it will be sufficient to spread in it very thin particles in order to see produced the phenomenon of the lateral propagation of light polarized according to the laws just mentioned. This is an important point which I sought to demonstrate in my previous researches‡, and of which I shall presently give fresh proofs.

But if, as I think, we are agreed upon this material fact, we again diverge as regards its interpretation, and even upon the cause of the phenomenon. M. Lallemand considers that, in the smoked surface, it is each molecule of carbon, or rather the atmosphere of æther condensed around each molecule, that determines the propagation of the light in all directions. For myself, I do

\* *Comptes Rendus de l'Académie des Sciences*, May 4, 1874, p. 1272.

† It is necessary to remark only that with a smoked surface the polarization is not complete—a fact, besides, often met with in the illumination of transparent bodies. I insisted on this point in my previous Note, and shall return to it further on.

I must here mention that MM. de la Prevostaye and Desains in their memoir "On the Diffusion of Heat" (*Annales de Chimie*, 1852, vol. xxxiv. p. 215 *et seq.*), published some results accordant with these laws, but without enunciating them in a complete manner. Sir D. Brewster, in his memoir entitled "On the Polarization of Light by Rough and White Surfaces" (*Philosophical Magazine*, 1863, vol. xxv. p. 344), did not study the case of black bodies.

‡ See *Archives des Sciences*, 1870, vol. xxxvii. pp. 150 *et seqq.*

not go so far, but continue to attribute it to the general fact of the reflection produced at the surface of separation between two unequally refracting media. Each particle of carbon, although very minute, is composed of a great number of molecules; it forms a minute body reflecting light, only, as its dimensions are very small, there is no annihilation by interference of the rays emitted in directions different from those determined by the ordinary laws of reflection: there is not specular reflection, but diffusion in all directions.

Let us look at some consequences of these two interpretations. Suppose a liquid having no power of illumination; then introduce some very fine particles of a solid body also having no power of illumination. If M. Lallemand's theory is accurate, the liquid, on ceasing to be homogeneous, will not receive the property of being illuminated, since neither of its constituents possesses it; while, according to my view, the trace of a luminous pencil must be marked in the liquid and present the usual phenomena of polarization, except in the quite exceptional case of the solid and liquid having the same index of refraction. The experiment is hardly realizable absolutely; but an approximation is possible. Water purified to the highest degree attainable, and containing only very few particles in suspension, has very little illumination-power; and calcspar has no sensible capacity of illumination, the trace of a pencil manifesting itself in the interior only by the slight red fluorescence of this body. Now, on suspending finely pulverized spar in water, and then filtering the liquor to separate the particles of too great a volume, I have found the power of illumination become much superior to that of the water alone\*.

On the other hand, if it is the molecules of the body themselves that produce the diffusion, it seems to me that the intensity of its manifestation should not depend on the refrangibility of the medium in which we operate. A smoked surface, for instance, whether it be in the air or in a more or less refracting liquid, should emit sensibly the same quantity of light. Now this is not what takes place; for it is easy to prove that the diffusing-power of lampblack is less intense in a liquid than in the

\* I cannot, however, give this experiment as entirely conclusive. The trace becomes incontestably more evident, and the polarization more pronounced; but the polarization is not complete, and there remains a residue of neutral light analogous to that which would be produced by an action of fluorescence. The colour of this residue is greenish, while the spar has a red fluorescence; besides, the proportion of solid particles is so trifling that it would be difficult to attribute a sensible fluorescence to them. Further, the trace presents very pronounced differences of colour, according to the angle under which it is viewed—a phenomenon manifested in other cases, and to which I purpose, one day, to return.

air. To perceive this it suffices to pour on the smoked surface a drop of alcohol, benzine, sulphide of carbon—in a word, of a liquid which moistens the lampblack; but in this case the polarization-phenomena are impaired\*. It is better to operate by immersing the smoked surface in a glass trough containing the liquid. This causes, it is true, a little perturbation owing to the circumstance that the liquids (such as alcohol and benzine) dissolve a substance deposited at the same time as the carbon, and become somewhat fluorescent; but this does not prevent the diminution of the intensity of the diffused light (without alteration of the polarization-phenomena) from being distinctly observed. Is it not probable that, if the index of refraction of the liquid were identically the same as that of the lampblack, there would be no light diffused?

It seems to me useless to insist further on this difference of interpretation, to which I attach only secondary importance. The question of knowing if the molecules can be regarded as by themselves effective centres of vibrations, or if the action of these molecules is transferred to the æther which surrounds them so as to modify its general density in the interior of a particle, is perhaps subtle and premature. To arrive at its solution, a very interesting part of the labours of M. Lallemand must certainly be taken into consideration; I mean his photometric researches. He has, in fact, shown that the intensity of the diffused light can be calculated by admitting that the vibration of the diffused ray is the projection of the incident vibration, and supposing that the vibratory motion is propagated with the same energy in all directions.

### *On the proper Colours of Bodies.*

We have seen that, at the time of the diffusion by a smoked surface, beside the polarized light there is always a residue of neutral light. To recognize it, we have only to view with an analyzer, under a visual angle of  $90^\circ$ , the surface illuminated by a pencil of light, or to examine it under any angle when the incident pencil is previously polarized.

I have indicated, in my previous Note, the reasons which prevent me from believing that this residue is due to fluorescence†. I think that it may be explained in part because the lampblack is not composed of pure carbon, partly because this

\* The conditions are then almost the same as when lampblack deposited on the hinder surface of a plate of glass is viewed through the glass, which is traversed by the incident pencil—a case of which we have to speak further.

† Nevertheless this case may present itself: M. Ed. Becquerel has in fact observed a phosphorescence in the lampblack deposited by certain flames; but a surface smoked at the flame of benzine is not phosphorescent.

substance does not realize absolutely the necessary conditions for complete polarization, but above all because multiple reflections must be produced. It is evident, on any theory, that a certain portion of the light diffused by a roughness of the surface must reach the neighbouring roughnesses, and there undergo diffusion a second time; and as the plane of polarization of the light after its first diffusion is generally different from that of the incident radiation, the twice diffused rays will be polarized in a different plane from that of the rays diffused once only.

In the case of the illumination of transparent bodies where particles are scantily disseminated in the medium, one can understand that the effect of these multiple reflections may be insensible; but on a smoked surface, where all the particles are contiguous, there is nothing surprising that the effect should become very appreciable.

Here again I regret being in discord with M. Lallemand, who explains this residue by a phenomenon of isochromatic fluorescence. I do not contest that certain bodies, as sulphide of carbon, may possess this faculty—that is to say, may emit by fluorescence rays of the same refrangibility as the incident light; I see no theoretic objection to admitting the existence of this property, which would be analogous to that of membranes vibrating in unison with all the sonorous undulations which strike them; but M. Lallemand gives it a generality the necessity of which does not appear to me to be proved. Indeed he attributes to it not merely the residue of neutral light observed in the diffusion produced by a smoked surface or other dull black bodies, but also the much more considerable proportion of neutral light diffused by white or coloured bodies. Isochromatic fluorescence is for him the cause of the proper colours of bodies.

The theory of the colours proper to substances appears to me well established, although many treatises on physics present large gaps in this respect: several do not mention it; others give it in an incomplete or erroneous manner\*. It will, perhaps, not be needless to explain it briefly, as I conceive it, taking into consideration the laws of polarization by diffusion, the study of which has recently made great progress.

Let us lay aside the phenomena of coloration which proceed from ordinary fluorescence (with change of refrangibility), of coloration by superficial reflection (metallic lustre), and of inter-

\* Verdet's *Cours de Physique à l'Ecole Polytechnique* explains it, in my opinion, very accurately but with sufficient brevity: vol. ii. p. 268. Dove gives it with many more details (*Darstellung der Farbenlehre*, Berlin, 1853). I have not made extensive bibliographic researches on the subject; but I remember that the theory in question is found in a great number of publications.

ference ; these phenomena are most frequently only superposed to those which are realized in a more general manner.

A black body is completely opaque. It is seen only by superficial reflection : if the surface is polished, the reflection is specular ; if the surface is dull, there is diffusion according to the laws we have ascertained concerning polarization. Between absolute polish and perfect absence of lustre we may have all the intermediate degrees.

A white body is transparent for every sort of luminous rays. It is visible, first, in consequence of superficial reflection, exactly as the black body ; but, in addition, there arrive at the eye rays which have undergone one or more interior reflections. If the body is polished and homogeneous, we have the well-known appearance of glass or colourless crystals. If the body is dull and homogeneous (ground glass), we have phenomena of surface diffusion as for black bodies, but with a twofold complication : the light which has penetrated the interior emerges again either directly or after interior reflection, undergoing diffusion by refraction ; moreover the light diffused exteriorly falls in part on the roughnesses of the surface, and may pass through them. If the body is polished but not homogeneous (porcelain), the surface reflection is specular ; but the rays which penetrate the substance are reflected or diffused in the interior, and a great portion of them emerge from the body. Finally, if the body is dull and not homogeneous, we have the combination of the two preceding cases.

It is easy to understand that the phenomena of polarization are completely disturbed as soon as the diffusion is no longer merely superficial. A very simple experiment makes this immediately intelligible. We have seen that, when a horizontal pencil polarized in a vertical plane falls on a plate of glass covered with lampblack, the visual plane being horizontal, and the visual angle  $90^\circ$ , we have only a residue of neutral light, whatever may be the position of the diffusing surface in relation to the incident pencil. If we turn the glass plate so that the pencil must pass through the glass in order to arrive at the lampblack, then the phenomenon is completely changed : the eye remaining in the same position, receives, instead of a neutral residue, light strongly polarized. The reason is easy to comprehend : the pencil of light, penetrating the plate (which is necessarily inclined upon its direction), is refracted and deviates ; the lampblack therefore does not receive a pencil making a right angle with the visual ray ; and therefore the light diffused in the direction of the latter must be polarized. To this cause of perturbation is joined the change of plane of polarization which the incident ray generally undergoes by its refraction,

and the polarization by refraction experienced by the diffused light in passing through the glass to arrive at the eye\*. This fact involves as a consequence that, if we operate exactly in the same manner, employing only a neutral incident pencil instead of a polarized pencil, the diffused rays will be much less polarized in the plane of vision than they are when the light arrives at the lampblack without passing through the glass. Phenomena of the same kind are generally produced when the light has penetrated into the body; and when the latter has no homogeneity and is not polished (chalk), very sensitive apparatus is requisite to discover a trace of polarization.

In coloured bodies the course of things is the same as in white bodies, except that, the body not being transparent to every kind of ray, it is only by superficial reflection or diffusion that the white light is sent back: all the light which penetrates into the interior to emerge again is coloured; and the colour is that of the rays which it permits to pass. It is natural, then, that the white light, diffused superficially, should be alone polarized, according to the laws of diffusion by a black body, while the coloured light, which has undergone internal reflection, is not polarized, or only partially so. From this results the fact, observed by several physicists, that if one views through an analyzer, under a visual angle of  $90^\circ$ , a coloured diffusing substance illumined by a pencil of natural light, the colour of the body appears very pure and saturated when the analyzer is turned so as to intercept the rays polarized in the plane of vision, while it is washed with white when the analyzer is in the reverse position or when it is viewed without an analyzer†. The experiment can also be made by illuminating the unpolished coloured surface by a horizontal pencil previously polarized in a vertical plane; in a horizontal visual plane, and under a visual angle of  $90^\circ$ , the colour then appears richer than in any other position‡. M.

\* When the incident pencil falls perpendicularly on the anterior surface of a plate of glass slightly smoked on its posterior surface, we may assure ourselves that there is no perturbation in the phenomena of polarization of the light diffused after its passage through the glass. In fact, in this case refraction modifies neither the direction nor the plane of polarization of the incident pencil, and, on the other hand, the diffused rays come direct to the eye.

† MM. de la Prevostaye and Desains interpret this fact by saying (with some reservation, it is true):—"It may hence be concluded that rays of different tints are not diffused in the same proportions and according to the same laws." Other authors content themselves with accounting for the colour of bodies by saying that they diffuse certain rays more than others: this is the expression of a fact, not an explanation.

‡ This experiment becomes very beautiful when it is effected in the following manner. A large pencil of solar or electric light is caused to enter a dark room, being concentrated by a lens of long focus; near the

Lallemand operated also by throwing a pure and polarized spectrum on the coloured diffusing surface: according to the position of the eye, the different diffused colours are perceived to be more or less polarized; and those which are the least polarized correspond to the proper colour of the body. But M. Lallemand attributes this to fluorescence, while, according to the theory which has just been explained, it is the result of absorption and depolarization by interior reflections.

In support of this theory must be mentioned first the fact that the colour of a body by diffusion is always the same as by transparence. I will here report some experiments which show it in a striking manner:—

A horizontal pencil of sunlight, polarized in a vertical plane, falls on the coloured diffusing surface. The observer views it under a visual angle of  $90^\circ$ , the plane of vision being horizontal: the colour, as we have said, appears very rich. But as the asperities of the surface are rarely minute enough for the diffusion to be perfect, and in certain cases the substance may be contained in a glass vessel, producing specular reflection, it is better to pass the diffused rays through a Nicol or a Foucault, stopping the rest of the polarized rays. The colour of the body then appears with the maximum of saturation and can be analyzed with the spectroscope.

It is convenient to choose for the operation of diffusion a substance the absorption-spectrum of which is discontinuous and characterized by bands.

Let us take smalt, for example. Although in powder its colour is much washed with white, because the thickness to be traversed by the light in the interior of the particles is too little to give rise to strong absorption, it is easy to distinguish in the diffusion-spectrum the characters attenuated of the absorption-spectrum of cobalt.

Let us now take some blood (the spectrum of which is so characteristic) and put it in a glass test-tube, or, still better, moisten with the blood the outside of the tube. Thanks to the Nicol prism placed in front of the spectroscope, the light reflected

point where the image of the sun is formed, where the pencil is narrowest, a large polarizer is placed. Then, at a distance of one or two metres, in the luminous divergent cone a bouquet of deep-coloured velvety flowers is placed, such as pansies or certain varieties of geraniums. The observer views the bouquet at a right angle with the incident pencil, while an assistant turns the polarizer. The tint of the bouquet then appears to pass through alternations of saturated colours and colours washed with white, which are very striking. The observer may also place himself in any position whatever, if he look through an analyzer which he keeps immovable while the polarizer is rotated, or *vice versa*.

specularly by the glass and by the surface of the liquid is intercepted, and scarcely any light passes but that diffused by the globules of the blood; with the spectroscope the two black bands characteristic of the spectrum of oxygenated blood are seen most distinctly. The experiment can also be made with filter-paper wetted with blood—but is then less conclusive, because the white fibres of the paper contribute largely to the diffusion.

In quitting this subject, let us observe that, to the explanation of the colour of bodies by fluorescence, objections can be made which it seems difficult to answer. A plate of obsidian glass roughed gives by diffusion a residue of non-polarized light; if it is due to fluorescence, why is it not seen when the obsidian is polished, in the same way as with a plate of uranium glass polished the light emitted by fluorescence is distinguished perfectly? and how is it to be explained that a transparent body (such as quartz) which manifests no fluorescence in its interior, or at its polished surface, can take isochromatic fluorescence when reduced to powder, or simply when its surface is roughed?

#### *A Study of some Crystallized Substances.*

I return now to the question whether a medium perfectly homogeneous and not fluorescent can be illuminated by the passage of a pencil of rays. This point appears to me important, because lateral propagation of light in this case is contrary to what has been generally admitted in the theory of undulations.

Crystallization is a very effective means of purifying substances; and good crystals present a high degree of homogeneity. Still this is by no means absolute; and it is well known that, except in very rare cases, the passage of a pencil of sunlight reveals defects (flaws or the presence of foreign corpuscles) in the interior of crystals that appear perfectly limpid in diffused light. The following are the results I have obtained in studying illumination in some crystallized substances:—

*Quartz.*—Of this I studied a great number of specimens\*.

They exhibit the most diverse properties with respect to illumination; I will mention a few examples of this.

1. Most frequently fine specimens of hyaline quartz, sufficiently pure to be employed in the construction of prisms or other optical apparatus, are not absolutely homogeneous; and when traversed by a pencil of sunlight, phenomena of illumina-

\* A portion of these belong to the Geneva Museum; but the most remarkable came from a collection of quartz objects acquired at the Vienna Exhibition by M. Rymtownt-Prince, who kindly permitted me to study them.



tion are produced. The trace of the pencil is visible; only it is in general unequal, and more marked in certain places than in others. On examining this trace with a lens or with a microscope, three cases can be distinguished:—

(a) Very often the trace is due to little defects of crystallization, to little flaws, which manifest themselves under the appearance of luminous strokes following one or two determinate directions\*. Under a vision-angle of  $90^\circ$  the polarization of the light thus diffused is complete, provided the defects of crystallization are *very minute*; when the flaws are large enough to be readily visible to the naked eye, the polarization is only partial. If the employment of the lens and of the analyzer be combined, these little defects of homogeneity, very apparent when the analyzer is in the position in which it lets pass the light polarized in the plane of vision, *totally cease to be visible* when the analyzer is rotated into the extinction-position.

(b) Sometimes the trace is due to minute bubbles or cavities which are discovered by means of a lens or a microscope. The light is here again completely polarized; the bubbles become invisible if viewed at a right angle to the pencil, with the analyzer suitably oriented.

(c) In some specimens, or in some parts of a specimen, I have not succeeded in resolving the trace with a low power of the microscope. But I have no doubt that, in this case again, it owes its origin to imperceptible defects or to foreign particles: indeed no limit can be assigned to their minuteness.

2. Some specimens of hyaline quartz, very pure and much rarer, are, so to say, destitute of the power of illumination.

(a) I possess a seal of Siberian quartz which is cut in such a way as very well to permit the observations: its general form is that of a six-sided prism with bases perpendicular to the edges. When placed in the dark room and traversed by a pencil of direct sunlight, no trace is to be seen. On concentrating the light by the process described above for the study of the reflecting-power of flames, taking at the same time the greatest precautions to avoid all false light, a slight trace can with difficulty be distinguished.

(b) Another seal, of Alpine quartz, the shape of which is rather less suitable for the observations, is incontestably illuminated in certain parts; but in others it has been impossible for me to see the trace.

3. A very beautiful seal of yellow Siberian quartz (false topaz), appearing quite limpid in diffused light, is brightly illuminated by a pencil of sunlight; the trace is bluish, and at first sight might be thought due to fluorescence. But on observing it with some care, the light emitted is recognized to be com-

\* I cited a case of this kind in the *Archives*, 1870, tome xxxvii. p. 155.

pletely polarized, and moreover not equal in every part of the crystal. Examination with the microscope reveals many little flaws in certain parts of the trace; but I did not succeed in resolving the whole of it\*.

I found in another seal of false topaz, from Brazil, the same properties, which are probably characteristic of this variety of quartz.

4. In *smoky* quartz, when it is not too dark, the trace is in general observed, but in very various degrees. When it is feeble, polarization is complete.

In a very fine brown specimen from Siberia, the defects of homogeneity manifest themselves, through transparency to diffused light, under the form of cloudy strata, indicating unequal distribution of the colouring-matter. With sunlight the trace is very marked, very incompletely polarized, and with a lens a multitude of defects and particles are distinguished. This incomplete polarization is a character always recognized when we operate on a liquid holding in suspension particles too numerous or of too great a volume.

5. A small specimen of amethyst cut in the shape of a prism with three sides, and with faces perpendicular to the edges, gave no visible trace in the greater part of the crystal; but in a few points small flaws are observed.

The study of these phenomena in quartz is often complicated by its property of chromatic polarization. Thus, by making the pencil of light pass, at a little distance from a face, parallel to the axis, and observing the trace with an analyzer, phenomena of coloration or depolarization can be seen, according to the orientation.

Rotatory polarization plays also an important part when the pencil is directed along the axis of the crystal. Here is a remarkable instance:—The second seal of false topaz above mentioned is cut so that its axis coincides with that of the crystal; it presents at its two extremities faces perpendicular to this axis. When a pencil of polarized light enters by one of these two faces to go out at the other, as the substance has a great power of illumination there is reproduced on a small scale the beautiful experiment realized by M. Lallemand when he employed liquids possessing rotatory power. The phenomenon shows itself in coloured fringes which are displaced in the interior of the crystal when the Nicol is rotated that polarizes the incident light. The

\* In truth, observation with the microscope is somewhat difficult: the luminous pencil, and consequently the trace, has always too large a section for the whole thickness to be brought to the point; the diffused light with which the entire field of the microscope is washed is opposed to the visibility of very small particles or defects.

first fringes, on the side where the pencil enters, are very bright and distinct; they grow confused and are effaced towards the other extremity.

*Calcareous Spar.*—I have found, like M. Lallemand, that fine specimens of Iceland spar present no power of illumination properly so called. The trace of a pencil of sunlight manifests itself solely by the slight red fluorescence of this substance; and no polarization is observed. But if we operate on certain crystals which exhibit minute defects, we can also obtain a white trace. The double refraction of the spar complicates the observation of the polarization-phenomena; yet, with some attention, it has appeared to me that the facts are in this case conformable to what could have been foreseen.

*Rock-salt.*—The only good specimen of rock-salt I have had at my disposal is a very fine prism belonging to the Physical Cabinet of the University of Geneva. In it a pencil of light produces a very slight trace, resolvable with the lens into small bubbles or cavities. The polarization is complete; and the defects are visible or disappear according to the orientation of the analyzer. This is the same as I have already stated for quartz.

In the other, less pure specimens which I have examined, the trace is visible, but unequal, and the polarization normal.

*Diamond.*—I had in possession for a few days some large diamonds which form part of the collection of the Duke of Brunswick, and which had been obligingly lent me by the municipality of Geneva. Unfortunately the season was very unfavourable, and I was only able to avail myself, for the observations, of a few moments during which the sun shone. Besides, the diamonds being cut as brilliants renders the observation very difficult: it gives rise to much false light; and on account of the reflection of the facets, one may readily confound the luminous trace with one of its images.

(1) A white diamond of 39 carats gave rise to a trace very visible and nearly white. The greater part of the light emitted by it is due to fluorescence; but I feel certain that another part is due to illumination properly so called; indeed the trace is partially polarized.

(2) Some yellow diamonds of 29, 31, 42, and  $80\frac{1}{2}$  carats gave rise to a very visible bluish trace, principally due to fluorescence, but also presenting partial polarization\*.

\* To observe the polarization-phenomena, I operated in the following manner. A pencil of sunlight, concentrated by a quartz lens of long focus, entered the dark room; it was polarized in passing through a Nicol, and then fell upon a screen pierced with a small aperture. A slender pencil

I do not hesitate to attribute these phenomena of polarization to foreign particles. We know, indeed, from Dumas and Stas\*, that diamonds leave a spongy residue after combustion; and Sir D. Brewster† recognized with the microscope cavities of various shapes in their interior.

*Ice.*—When very clear and compact, it exhibits very little capacity of illumination. When floating in water in a large glass vessel through which the pencil of rays passes, the trace is very pronounced in the water, but almost invisible in the ice. Cutting a piece of ice into a suitable shape, I had no difficulty in distinguishing in it the trace, which, when viewed through a lens, is seen to resolve itself into minute particles. It is *much less visible* than that of the purest water I succeeded in obtaining by distillation‡; its polarization is complete§.

*Alum.*—A crystal of alum, in which I had faces cut at right angles, gives a trace in the parts where flaws are present, but in other parts does not appear to have any capability of illumination.

*Gypsum.*—I cite from memory a specimen of gypsum from the collection of M. Alph. Favre. I examined it, a long time ago, with the oxyhydrogen light only, and did not recognize in it any trace.

The whole of these observations appear to me to well establish:—

1st. That in non-fluorescent crystals the crystallizable matter by itself is destitute of illuminability.

2nd. That crystals which possess the faculty of being illuminated by returning polarized light laterally, owe that property either to the presence of foreign particles or to defects of crystallization.

of polarized light was thus obtained, which I caused to enter into the diamond through the large front face of the brilliant, and to emerge through the parallel facet (the collet) which generally terminates the rear of a brilliant. The trace was then viewed with a Nicol, through one of the inclined faces that form the posterior pyramid. In these conditions, on turning the Nicol, differences of intensity are observed if the trace is partially polarized.

\* *Annales de Chimie*, 1844, vol. i. p. 15.

† Trans. of Royal Society of Edinburgh, vol. xxiii. p. 1.

‡ For the purification of water by distillation, see *Archives*, 1870, vol. xxxvii. p. 146.

§ I am here speaking of the naturally formed ice of ponds; there are great differences, according to the specimens. I recall here that Tyndall indicated water proceeding from the melting of ice as the most exempt from particles and illumination-power that he could obtain.

VII. *On the Spectrum of the Aurora.* (Extract from a Letter from Professor A. S. HERSCHEL to R. H. SCOTT, Esq., F.R.S.\*)

..... THE paper by Ångström, noticed in 'Nature' (vol. x. No. 246, July 16, 1874), was a rare legacy of his last days to spectroscopists of auroras. Nothing more conclusive and satisfactory, that I know of, has been written on the subject; and little more will be done now, I expect, by future observers than to verify his conclusions and to extend the research in the direction that he points out, in its more numerous details.

The spectrum of the aurora is no doubt in the main the same as that of the pale blue light round the negative pole in an air or nitrogen vacuum-tube, with the induction-spark passing through it. There are so many well marked lines in this spectrum that, looking at Ångström's representation of them, it is probably owing to the insignificant appearance of that part of the vacuum-spark that its proper spectrum has not been more frequently studied with reference to the aurora, as Ångström seems to have done by an experiment specially adapted for the purpose.

There are several forms or modes (apparently four or five) of electrical discharge through rarefied gases†. When very much rarefied, air transmits the electricity so as to discharge the Ruhmkorff poles without a spark. In that state there is still a glow of heated air round both poles, which increases in size and length along the tube as the air-pressure is increased, faster round the positive than round the negative pole. This has been accounted for by showing that the air offers far greater resistance to the passage of electricity when it surrounds a cathode or negative, than when it surrounds an anode or positively electrified pole. The difference becomes more obvious as the pressure and density of the gas are increased. The negative glow shrinks into a very small space, while the positive brush extends through nearly the whole length of the tube, abolishing at last the dark space that at very low tensions separates the two lights from each other. At pressures not exceeding one or two millimetres the positive glow is stratified; but if the pressure is increased it becomes continuous; and if the air-pressure amounts to that of  $\frac{1}{4}$  or  $\frac{1}{2}$  an inch of mercury, or upwards, it again gathers into

\* Communicated by R. H. Scott, Esq.

† An examination of these with revolving mirrors, by A. Wüllner, at Aix la Chapelle, appeared in the "Jubelband" of Pogendorff's *Annalen* this year at the same time as Ångström's paper in that volume, which also contains some other tracts (by A. de la Rive and others) tracing the effects of magnets and of metallic vapours in augmenting the discharge through air.

somewhat larger light clouds; and at about 1 or 2 inches of barometric pressure a spark passes between the poles. This spark is red; it scarcely diminishes the strength of the concomitant glow discharge; and it is far less luminous than the white spark which begins to appear at 5 or 6 inches of pressure, and may often be seen at first broken up along its length into parts which are alternately white and red. The spectra, like the general appearances, of these two forms of the spark are quite distinct.

I do not know if these several phases of the *positive* part of the discharge have all been examined spectroscopically. They pass into each other according to the shape and size of the tube or flask, as well as the air-pressure; and it is difficult to say how much of each is concerned in those observations which have been made of air-spark spectra in comparisons with the aurora. No one, so far as I know, has compared with it the *negative*-glow spectrum so fully as Angström has now done; and it seems very probable that its peculiar fitness for the comparison has been overlooked—the feat of filling a bottle with the negative glow discharge being certainly a novelty; if it is really true that he succeeded in obliterating the positive brush entirely in its favour.

The next remarkable novelty in the paper is the way in which he proposes to account for the “citron” line of auroras; for there is evidently nothing of the kind in the negative glow, however well that answers to all the secondary facts of faint blue, red, and greenish lines. If oxygen and its compounds are (as has, I believe, been lately shown) strongly *fluorescent*, Tait and Dewar have also proved, as shown by some of their experiments this year, that they also possess powers of *phosphorescence*—Geissler tubes shining for some time after the spark has passed through them, from the production of ozone during the discharge. When one of the globes of a phosphorescent “garland” tube was heated over a Bunsen flame, that globe which was heated did not shine after the spark had passed, apparently because, as we know, a very little heat is sufficient to destroy ozone. Whatever the way may be in which the ozone or otherwise electrified gas remains self-luminous after the discharge, it seems very reasonable to suppose some action of the same kind (perhaps, as Angström says, simply fluorescence) as common in all auroras, and that this produces the well-known auroral line.

Pocket spectroscopes can, of course, do nothing further to fix the position of the citron line; nor can they alone fix very exactly the places of any of the fainter ones. But as every aurora shows this strong monochromatic light, it might be used to bring out a row of punctures transverse to the slit, as a divided scale in the field of view whereby to map the fainter lines, or at any rate

to recognize those which appear most frequently. For this purpose they should be made large, and the slit should be a wide one. For ordinary miniature spectrosopes, two holes on the red and five on the blue side of the slit  $\frac{1}{40}$  or  $\frac{1}{50}$  of an inch apart, would suffice for recognitions and even for very useful measurements. The jaws of the slit can be cut with a fine saw across the middle about  $\frac{1}{10}$  or  $\frac{1}{8}$  of an inch deep each way; and a piece of copper foil, provided with the row of holes and a sufficiently wide slit across it, can be fastened to one of them inside, opposite to the crosscut and adjoining the edges of the spectroscope jaws.

Some other means may be found of piercing the jaws of a pocket spectroscope at regular intervals; but as a simple plan I have found this very efficient, in finer divisions, for laboratory use. The holes are pierced at  $\frac{1}{150}$  of an inch apart; and thirty of them include the whole visible spectrum. Sodium-light, which is common in laboratory flames, exhibits the punctures with admirable distinctness; and each fifth hole being punched double, the scale is very easily read off. There are ten holes on the red, and twenty on the blue side of the slit. If the mechanical difficulty of perforated jaws could be overcome, nothing perhaps could be better suited for examining auroras than a pocket spectroscope so prepared with a few close but clear and tolerably open holes on each side of the slit.

The secondary auroral lines can only be seen (in small spectroscopes) with a pretty broad slit; and the strength of the yellow line might then prove embarrassing. I would abolish it, if so, by a blue\* glass nearly covering one half, and a red glass the other half of the slit—the blue and red parts of the spectrum respectively, not in its immediate neighbourhood, being freely transmitted. The slit might also be made longer than usual for auroral study.

I have been here supposing that special spectroscopes would be provided for Arctic observers. But it is quite certain that much may be done with common pocket spectroscopes without any such provision. They should have adjustable slits and good dispersion, as the secondary lines are faint; and though abundant enough in the blue to make the spectrum there pretty luminous, they can only be individualized by varying the slit-aperture. On the only occasion when I have seen this spectrum (in February 1872) they seemed to run into each other, and presented a light so nearly continuous in the blue part that, although the slit of the Browning's pocket spectroscope which I was using was extremely fine, and was focused on the

\* Some care would be necessary in selecting the blue glass, as these generally transmit a yellow ray closely corresponding with the auroral line.

yellow line, no interruption or appearance of lines could be made out. It was probably also through not opening the slit that I missed seeing a red line which another observer, using a similar instrument and looking with me at the aurora, saw very plainly. Although its red colour was intensely brilliant, I failed to see the slightest trace of light on the red side of the yellow line. Had I opened the slit, or perhaps opened and closed it alternately (as the yellow line, though fine, was still very bright), the result would probably have been different.

I send with this a copy of the Plate of spectra accompanying Ångström's original paper (see fig. p. 71); and I can confirm the appearance of the negative or "cathode" spectrum which he gives, from the results of some examinations of it which I have lately made. On projecting the recorded lines in wave-lengths, there is a very exact agreement with the chief lines and shadings as figured in the Plate. Some fainter lines, however, are visible, which Ångström has perhaps omitted purposely, to avoid encumbering the drawing. As regards the aurora spectrum, considering the numbers of lines which have been mapped and measured, I am not so well prepared to say how complete Ångström's selection of its principal ones may be. It may, I think, be taken for granted that his map includes every line of whose existence, approximate place, and brightness there is really no doubt, and that it does represent the *normal spectrum* of the aurora when sufficiently bright. During the years 1871 and 1872 there were several *résumés* of the subject, accompanied with new measurements, in Poggendorff's *Annalen* and the 'American Journal of Science' (by Vogel, Barker, and others), with which, from his comments on them, Ångström was evidently familiar. Adopting his selection, therefore, and the descriptions which he gives, from his own and other observers' notes, of relative brightness and appearance, I have endeavoured to condense the information in the annexed Table as a guide for further observation.

Professor Piazzi Smyth, who has given much attention to the auroral spectrum, has published, in the introduction to vol. xiii. of the 'Edinburgh Astronomical Observations,' a set of simple comparison spectra, with notes of *desiderata*, which would be of great service to observers well furnished with instrumental means and applying them to measurements of the aurora; and something similar would very much assist observers using direct-vision spectroscopes to map their spectra, where auroras are frequent and of great brightness, in high latitudes.

Hoping that these notes may be of use for the purpose of comparison with occasional observations of auroras,

I remain, &c.,

Newcastle-on-Tyne, July 24, 1874.

(Signed) A. S. H.



*Positions and General Characters of Principal Lines in the Auroral Spectrum, according to Ångström.*

Red . . 1. *Brightness* 0 to 4 or 8. *Wave-length* 6300.  
*Relative position.* Atmospheric absorption-line  $\alpha$  near C in the solar spectrum.

*General description of source and frequency.* Seen chiefly, if not only, in red auroras; a clearly defined line, sometimes intense; no other red line visible.

*Identification with lines of electrical air-spectra.* Coincides with a red band in the negative-glow discharge.

Yellow or citron-green. }  $\alpha$ . *Brightness* 25. *Wave-length* 5570.

*Position.* Second separable line in the first or citron band of blue gas-flame spectrum.

*Description &c.* The most characteristic auroral line; constant and conspicuous in all auroras; not divisible; sharp and bright.

*Identification &c.* Not identified; possibly a phosphorescent or fluorescent light emitted when air is subjected to the action of electrical discharge.

Greenish blue or blue. {  $\beta$ . *Brightness* 2 or 0? to 6. . . . *Wave-length* 5225.  
                                    $\beta a$ .    ,,    0-8 (increases with red line) }    ,,    5170-5190.  
                                    $\beta b$ .    ,,    2 or 0? to 8. . . .    ,,    5000.  
                                    $\beta c$ .    ,,    0 to 4? . . . . .    ,,    4820-4870.

*Position.*  $\beta$  and  $\beta a$  closely adjoin the solar line  $b$  and the second or green band of the blue gas-flame spectrum.  $\beta b$  is at  $\frac{1}{2}$  ( $b$ , F); and the line or lines  $\beta c$  are near F.

*Description &c.* The first three are distinct lines; the first most frequently observed; the second and third less commonly; lines in the fourth place ( $\beta c$ ) noted by Alvan Clark, jun., Barker, and Ångström.

*Identification &c.*  $\beta$ ,  $\beta b$  coincide with lines in the negative glow,  $\beta b$  that of nitrogen in the nebulae;  $\beta a$  with a constant strong line in the spark-discharge. The latter and  $\beta c$ , it may be, are only seen in auroral streamers of low elevation.

Full blue. { 4. *Brightness* 3-6 (fainter with red line) . . . . } *Wave-length* 4665-4740.  
                                    $\gamma a$ .    ,,    . . . . .    ,,    4630-4665.

*Position.* Middle and latter half of the third or blue band in the blue gas-flame spectrum.

*Description &c.* A double band, consisting of two lines; the first rather more frequently noted than the second in auroral spectra.

*Identification &c.* The principal line and its companion agree well in position with the principal band in the negative-glow spectrum.

Indigo, blue and violet.	}	5.	Brightness 0-6.	Wave-length 4285.
		6.	" ..	" 4110.

*Position &c.* 5 coincides nearly with G and with the fourth or indigo band of the gas-flame spectrum; 6 is between G and H, near the hydrogen line *h* in the solar spectrum.

*Description &c.* 5 is a frequent but somewhat difficultly visible line; and, from its position, it is possibly the limit of vision for pocket spectroscopes; 6 was measured once by Lemström at Helsingfors.

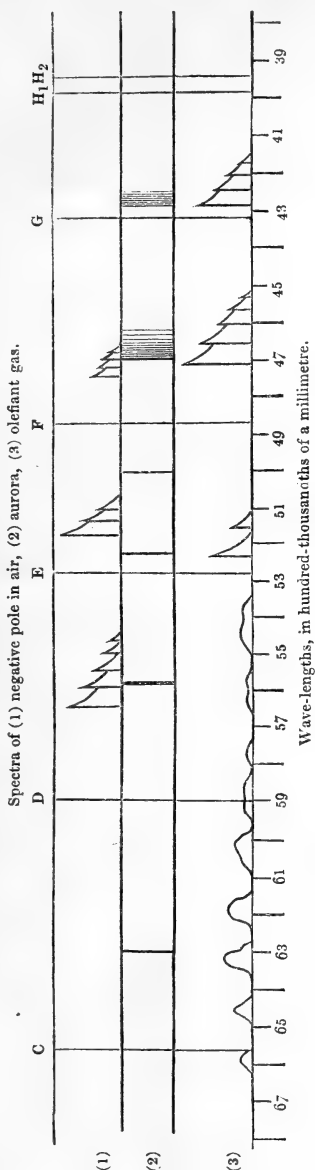
*Identification &c.* 5 corresponds exactly with a strong band in the violet in the negative-glow spectrum.

#### *Remarks and Suggestions.*

The general character of the subspectrum appears to be a series of bright lines, bands, and shadings, more or less dimly visible on a faint field of light in the blue region of the spectrum, the greatest concentration occurring apparently most frequently at about the positions stated above. They arise, according to Ångström, from discharges of electricity from the denser to the more rarefied strata of the upper air, producing there on a great scale what is seen in artificial discharges of electricity in rarefied air as a blue cap round the negative pole. The appearance in the aurora of only one red line in the place of the many red bands of the negative glow, scarcely less bright than the principal one, is remarkable; and fresh observations are very desirable to confirm it, or to detect other red lines if they exist. Very red auroras should be examined with a wide slit, covered (if of advantage) with light-red glass to shut off all other light as much as possible.

Mixed with the lines of the *negative* glow, Ångström supposes that lines of the positive disruptive spark or brush discharge may appear in flashing auroras, especially near the base or arch

Ångström's representation of the Spectrum of the glow discharge round the negative pole of Air-vacuum Tubes, and its comparison with the Spectrum of the Aurora.



as distinguished from the tops of the streamers, giving to the sub-spectrum a different appearance according to the strength and agitation of the streamers: this may perhaps be traceable in the appearance and disappearance of the lines 3 a, 3 c, and perhaps of other faint lines, whose positions should be noted. Such lines should also be searched for in quiescent parts, such as stationary auroral bands and the tops of very bright streamers.

A correct recognition of some one or more of the lines described above, other than the citron line, is, however, of chief importance in observing with small spectroscopes, as the leading lines themselves must supply the only standard intervals of comparison for eye-estimations of such faint spectra.

VIII: *Notices respecting New Books.*

*Nature Series. Polarization of Light.* By WILLIAM SPOTISWOODE, M.A., LL.D., F.R.S., &c London: Macmillan and Co. 1874 (crown 8vo, pp. 129).

THIS work contains an admirably clear and exact account of the phenomena of Polarized Light. The author explains, in the first place, the various ways in which light is made to undergo the process of plane polarization (by passage through a doubly-refracting crystal and by reflexion and refraction by glass), and then describes the double-image prism, Nicol's prism, and Norremberg's apparatus. The subjects of the interference of plane-polarized light, the methods of producing circularly polarized light, and the interference of circularly polarized light are next discussed at considerable length with reference to pencils of parallel rays. These subjects fill two thirds of the volume; but, as well as the main subject, several collateral points of great interest come under notice in the course of the discussion: such are the various forms of the saccharometer, Sir C. Wheatstone's apparatus for producing circularly polarized light by reflexion at a metallic surface, and exhibiting the effects of passing light in that state through crystal films, the phenomena resulting from the action on polarized light of glass when unequally cooled, or when in a state of stress, the phenomenon of atmospheric polarization, the polar clock, &c. The student who has made out this part of the volume will be able to understand easily the account which follows of the results arising from the use of a pencil of divergent rays, and the beautiful phenomena of coloured rings produced by the action of various crystals on such a pencil. In several places the author notices the results of an examination of the spectrum of the pencil of interfering light which issues from the analyzer; and a good deal of attention is paid to the production of complementary colours by polarized light. In fact the last chapter of the volume is a reprint of the author's paper "On Combinations of Colour by means of Polarized Light," originally published in the 'Proceedings of the Royal Society,' vol. xxii. p. 354.

It will be seen from the above brief account of its contents that the work before us passes in review all the main points of interest in the subject. The author speaks of his book as "a talk rather than a treatise on polarized light," and says that it contains "the substance of lectures delivered at various times to my work-people." It is therefore so far a popular book, that the subject is discussed without the aid of mathematical symbols; and doubtless, when the experiments described were actually exhibited, the lectures would be very interesting to any intelligent audience. This, however, does not prevent the book from being decidedly hard reading; and it would be easy to point out passages which could not be fully understood by a reader wholly without the mathematical learning which the author has at command. On the other hand, a reader who already has some acquaintance with the mathematical treatment of the subject will find the time usefully spent which he de-

votes to the study of a work like the present, which gives with great clearness, accuracy, and brevity the facts of the subject clothed, as far as may be, in the language of daily life.

The illustrations are sufficiently numerous: some of them are little more than diagrams; others are elaborate drawings of instruments, and are very good, *e. g.* those on p. 60 and p. 102. There are also two whole pages of coloured figures (which are very beautifully done), showing the rings and brushes produced by polarized light in the case of six crystals, two complementary figures for each crystal. In conclusion we can cordially recommend the book to the somewhat select class of readers who take an intelligent interest in this beautiful branch of science.

### IX. *Proceedings of Learned Societies.*

#### GEOLOGICAL SOCIETY.

[Continued from vol. *xlvi*. p. 546.]

February 4, 1874.—His Grace the Duke of Argyll, K.T., F.R.S., President, in the Chair.

THE following communications were read:—

1. "The Physical History of the Valley of the Rhine." By Prof. A. C. Ramsay, LL.D., V.P.R.S., Vice-President.

The author first described the general physical characters of the valley of the Rhine, and discussed some of the hypotheses which have been put forward to explain them. His own opinion was that during portions of the Miocene epoch the drainage through the great valley between the Schwarzwald and the Vosges ran from the Devonian hills north of Mainz into the area now occupied by the Miocene rocks of Switzerland. Then after the physical disturbances which closed the Miocene epoch in these regions, the direction of the drainage was reversed, so that, after passing through the hill-country between the lake of Constance and Basel, the river flowed along an elevated plain formed of Miocene deposits, the remains of which still exist at the sides of the valley between Basel and Mainz. At the same time the Rhine flowed in a minor valley through the upland country formed of Devonian rocks which now constitute the Taunus, the Hunsrück, and the highland lying towards Bonn; and by the ordinary erosive action of the great river the gorge was gradually formed and deepened to its present level. In proportion as the gorge deepened, the marly flat Miocene strata of the area between Mainz and Basel were also in great part worn away, leaving the existing plain, which presents a deceptive appearance of having once been occupied by a great lake.

2. "On the Correspondence between some Areas of Apparent Upheaval and the Thickening of Subjacent Beds." By W. Topley, Esq., F.G.S., Geological Survey of England.

The author referred to many instances in which beds have unequal development, being much thicker in some places than in others; and the main object of his paper was to show that such thickening and thinning of beds has an important effect in producing the apparent dip of overlying beds. The thinning of any one bed may

have an appreciable effect in producing or increasing its own apparent dip ; but where a whole series of beds thin constantly in one direction, the amount of the dip of one of the higher beds, due to the *sum of the thinnings of the underlying beds*, is often very considerable.

In illustration of this the author indicated the Lower Jurassic rocks between Leckhampton Hill and Burford. The Inferior Oolite, and the Upper, Middle, and Lower Lias thin out rapidly to the east along this line ; the base of the Middle, Lias is nearly a horizontal line, the easterly "dip" of the Great Oolite being due to the easterly thinning of the Middle and Upper Lias and the Inferior Oolite. The base of the Lower Lias has a *westerly* dip.

It is generally supposed that the dip of any bed is due to great movements of the earth's crust ; from the facts mentioned the author argued that our inferences as to such movements will vary according to the beds which happen to be exposed at the surface. In the example given we assume a westerly upheaval because we see the Great Oolite dipping to the east. If over this area the whole of the higher strata had been removed down to the Middle Lias, we should perceive the beds to be flat ; if the denudation had exposed the base of the Lias, we should probably suppose that along this line there had been an easterly upheaval.

Under London the entire series of strata between the Palæozoic rocks and the base of the Upper Cretaceous is absent ; as we recede from the London Basin the intermediate beds necessarily come in and gradually thicken, producing the dip of the Cretaceous beds towards the London Basin.

The Palæozoic rocks under London are about 800 feet below sea-level. We now know, by the sub-Wealden boring, that under the centre of the Weald the Palæozoics are also below sea-level. Supposing that they should be found at about the same depth as at Kentish Town, then the Palæozoic floor will be approximately a straight line, whilst we know that the whole of the Wealden and other cretaceous beds dip to the north, their dip being thus wholly accounted for by the gradual thinning out of all the beds as they approach London. In the case of the Weald, some of the strata are of freshwater origin ; we must suppose that the area of water within which they were deposited had some limit to the north, and that the Palæozoic floor, which is now approximately flat, rose up to the north as a bounding ridge. But even if this be so, it is evident that the present dips are no exact measure of the amount of upheaval which the beds have undergone.

Other examples were quoted in which the observed general dip corresponds in direction with the known or inferred general thinning ; and it was shown that in all such cases we are liable to serious error in inferring the amount of upheaval from observed dips.

It is, however, evident, from the faults intersecting strata, that upheavals and disturbances have taken place ; but unless we assume every bed to have been deposited on a perfectly horizontal plane, we cannot infer the amount of such upheaval from the present position of the bed. In all cases we must take into account the actual or possible thinning of underlying beds.

The beds which support Geological Basins frequently thin towards the centres of those basins, thus producing, wholly or in part, the basined form of the strata. It was, however, shown that the beds of the basins themselves frequently thicken towards the centre of the basins.

February 25th.—John Evans, Esq., F.R.S., President, in the Chair.

The following communications were read:—

1. "Geological Notes on a Journey from Algiers to the Sahara."  
By George Maw, Esq., F.L.S., F.G.S.

The author commences by describing the details observed on his journey from Algiers to L'Aghouat, on the borders of the Sahara. The distance traversed was 285 miles, or about 210 miles in a straight line, and in a direction nearly north and south. No eruptive rocks were observed. The oldest rock is a boss of mica-schist and gneiss behind the city of Algiers; it forms a low anticlinal, with a N. and S. strike. The pass through the gorge of the Chiffa in the Lesser Atlas shows hard slaty rocks dipping S. at a high angle; they are repeated as an anticlinal on the south side of the higher part of the Tell plateau, and are probably Mesozoic. In the plain separating the Tell from the Hauts Plateaux, and on the south side of the latter, red and yellow sandstones form anticlinals; these rocks resemble the Bunter in mineral characters, and are overlain by red marls resembling the Keuper. In the northern escarpment of the Hauts Plateaux saliferous marls are exposed, interstratified between the sandstones and below the red and grey marls. Crystals of salt and gypsum are intimately mixed with the grey marls; and the so-called "Rochers de Sel" are capped with great blocks of rock tumbled about in confusion, the position of which the author ascribes to the failure of support due to the solution of the salt in the underlying salt-marls. A thin series of bright red and green marls is seen to overlie the Red Sandstones in several places; and above this is an immense series of dark grey marls, interstratified with argillaceous-calcareous bands, forming a great synclinal of the Hauts Plateaux, and a contorted mass on the Tell plateau. These are probably cretaceous. At L'Aghouat they are overlain by fossiliferous beds, probably of Miocene age. Other Tertiary beds observed are soft yellow calcareous freestones on the flanks of the promontory of Algiers and of the Lesser Atlas, and some red and grey marls and ferruginous freestone capping the Tell plateau, the former at a height of 100–900 feet, and the latter of 2500–4000 feet above the sea-level. The plain of the Mitidja, between the Lesser Atlas and Algiers, consists of grey loam with shingle-beds, of post-tertiary age. A similar loam covers the great plain of the northern Sahara, and rises to a height of 2700 feet. Raised beaches occur on the coast up to an elevation of 600 feet above the sea-level; and similar beaches are found inland, south of the Tell plateau, at a height of 2000 feet.

The oldest land in the line of section is the anticlinal of mica schist near Algiers, the strike of which is nearly at right angles to that of the other rocks. The upheaval of the Mesozoic rocks was contemporaneous with the first upheaval of the Lesser Atlas; it was followed by a long period of denudation, and this by a subsidence of

at least 3000 feet in Tertiary times, during which the Miocene deposits were formed. The Tell plateau was thus elevated at least 4000 feet, and the district north of the Lesser Atlas at least 1000 feet, the north face of those mountains probably marking a post-tertiary line of fault of 3000 feet. This operation was followed by a long period of denudation, and this by a post-tertiary depression, which the author terms the "Sahara submergence," after which the land was reelevated at least 3000 feet, but perhaps considerably more. A gradual subsidence appears to be still taking place.

2. "On the Trimerellidæ, a Palæozoic Family of the Palliobranchs or Brachiopoda." By Thomas Davidson, Esq., F.R.S., F.G.S., &c., and Prof. William King, Sc.D.

In this memoir the authors describe in detail certain Brachiopoda, for which they propose to establish a distinct family, discuss the characters and affinities of the family, and indicate certain geological considerations which arise from their study of its members. The first known species were described in 1853 under the names of *Obolus Davidsoni* and *O. transversus*; but in 1862 Mr. Billings described an allied form as constituting a new genus called *Trimerella*. With this *Gotlandia* of Dall (1870) is identical. In 1871 Prof. Hall proposed the new genera *Rhynobolus* and *Dinobolus*; and in the same year Mr. Billings established the genus *Monomerella*. *Rhynobolus* is regarded by the authors as a synonym of *Trimerella*; and several other proposed genera being similarly cancelled, the authors retain only the genera *Trimerella*, *Dinobolus*, and *Monomerella* as constituting their family Trimerellidæ.

The Trimerellidæ are described as having a calcareous shell, generally massive, with the umbo of the pedicle-valve often large, pointed, solid or hollow; area usually of considerable size, with a large solid deltidium; hinge of both valves slightly dentary; in the interior of each valve there is a more or less elevated platform, longitudinally placed, and either solid or doubly vaulted; and from the middle of its anterior end a median plate occasionally projects into the anterior half of the valve, especially in the brachial valve.

In discussing the affinities of the new family, the authors enter in considerable detail into the arrangement and functions of the muscles of the Brachiopoda, and show, from the muscular indications and other characters of the Trimerellidæ, that they are most nearly allied to the Lingulidæ, although presenting characters of sufficient importance to warrant their separation as a distinct family.

As far as is at present known, the Trimerellidæ are confined to the Cambro-Silurian and Silurian systems; but the authors indicate the probability that in the Cambrian or early Cambro-Silurian rocks a generalized form will hereafter be detected, bringing *Discina*, *Lingula*, and *Obolus* into close relationship, as regards their myology, with each other and with *Dinobolus*. Such a form would constitute the root from which the Trimerellidæ have originated.

The genera and species described are as follows:—

Genus 1. *Trimerella*, Billings (1862). Sp. 1. *T. grandis*, Bill.; 2. *T. acuminata*, Bill.; 3. *T. Lindströmi*, Dall; 4. *T. Billingsii*,



Dall ; 5. *T. ? galtensis*, Bill., = *minor*, Dall ; 6. *T. ohioensis*, Meek ; 7. *T. Dalli*, Dav. & King ; 8. *T. wisbyensis*, Dav. & King.

Genus 2. *Monomerella*, Billings (1871). Sp. 1. *M. prisca*, Bill. ; 2. *M. Walmstedti*, Dav. & King ; 3. *M. Lindströmi*, Dav. & King ; 4. *M. orbicularis*, Bill.

Genus 3. *Dinobolus*, Hall (1871). Sp. 1. *D. Conradi*, Hall ; 2. *D. Davidsoni*, Salt. ; 3. *D. canadensis*, Bill. ; 4. *D. transversus*, Salt. ; 5. *D. Woodwardi*, Salt. ; 6. *D. magnificus*, Bill. ; 7. *D. Schmidtii*, sp. n.

The authors further discuss the characters of Professor Hall's *Lingulops Whitfieldi*, which they regard as in some respects intermediate between the Lingulidæ and Trimerellidæ, and describe under the name of *Chelodes Bergmani* a fossil sent to them by Dr. Lindström under the impression that it was a Trimerellid. They indicate its points of resemblance to *Trimerella*, but think that it really belongs to the section of the Cœlenterata represented by *Calceola* and *Goniophyllum*. The fossil is from the isle of Gothland, and was obtained from a formation equivalent to the Aymestry limestone.

### X. Intelligence and Miscellaneous Articles.

#### PERMANENT ICE IN A MINE IN THE ROCKY MOUNTAINS.

BY R. WEISER, OF GEORGETOWN, COLORADO.

GEOLOGISTS have been not a little perplexed with the frozen rocks found in some of our silver-mines in Clear Creek Co., Colorado. I will first give a statement of the facts in the case, and then a theory for their explanation.

There is a silver-mine high up on McClellan Mountain, called the "Stevens Mine." The altitude of this mine is 12,500 feet. At the depth of from 60 to 200 feet the crevice matter, consisting of silica, calcite, and ore, together with the surrounding wall-rocks, is found to be in a solid frozen mass. McClellan Mountain is one of the highest eastern spurs of the Snowy Range ; it has the form of a horseshoe, with a bold escarpment of felspathic rock near 2000 feet high, which in some places is nearly perpendicular. The Stevens Mine is situated in the south-western bed of the great horseshoe ; it opens from the north-western. A tunnel is driven into the mountain on the lode, where the rock is almost perpendicular. Nothing unusual occurred until a distance of some 80 or 90 feet was made ; and then the frozen territory was reached, and it has continued for over 200 feet. There are no indications of a thaw summer or winter ; the whole frozen territory is surrounded by hard massive rock, and the lode itself is as hard and solid as the rock. The miners being unable to excavate the frozen material by pick or drill to get out the ore (for it is a rich lode, running argenteriferous galena from 5 to 1200 ounces to the ton), found the only way was to kindle a large wood fire at night against the back end of the tunnel and thus thaw the frozen material, and in the morning take out the disintegrated ore. This has been the mode of mining for more than two years. The tunnel is over 200 feet deep, and there is no diminution of the frost ; it seems to be rather increasing. There is, so far as we can see, no opening or channel through which the frost could possibly have reached such a depth

from the surface. There are other mines in the same vicinity in a like frozen state.

From what we know of the depth to which frost usually penetrates into the earth, it does not appear probable that it could have reached the depth of 200 feet through the solid rock in the Stevens Mine, nor even through the crevice matter of the lode, which, as we have stated, is as hard as the rock itself. The idea, then, of the frost reaching such a depth from the outside being utterly untenable, I can see no other way than to fall back upon the Glacial era of the Quaternary. Evidences of the Glacial Period are found all over the Rocky Mountains. Just above the Stevens Mine there are the remains of a moraine nearly a mile long, and half a mile wide. The débris of this moraine consists of small square and angular stones, clearly showing that they have not come from any great distance. And just over the range, on the Pacific slope, there are the remains of the largest moraine I have ever seen, consisting of felspathic boulders of immense size. I conclude, therefore, that it was during that period of intense cold that the frost penetrated so far down into these rocks, and that it has been there ever since, and bids fair to remain for a long time to come.—Silliman's *American Journal*, December 1874.

#### ON THE MIXTURE OF COLOURS IN BINOCULAR VISION.

BY W. VON BEZOLD\*.

The Author has succeeded in clearing up and reconciling the divergent observations of different observers on the mixed colours produced when the two eyes receive light of different colours. Some, as Dove or Ludwig, assert most positively that it is possible to obtain a combined colour by the binocular fusion of two images of different colours; while Franke, Helmholtz, and others advance precisely the contrary.

According to the Author, the combined tint is obtained when, with one and the same accommodation, the differently coloured surfaces are both at the distance of distinct vision. When this is not the case, there is a struggle between the two visual fields, and one or the other prevails.—*Bibliothèque Universelle, Archives des Sciences*, No 202, p. 184.

#### EXPERIMENTAL STUDIES ON THE ELECTRICAL RESISTANCE OF METALS AND ITS VARIATION UNDER THE INFLUENCE OF TEMPERATURE. BY RENÉ BENOIT†.

Resuming the important question of the electric conductivity of metals, M. Benoit first measured very accurately the specific resistance of a number of them at 0° C. For this he operated comparatively with two different methods—that of the differential galvanometer, and that of the Wheatstone bridge; and he made numerous determinations on various specimens of each metal. The following Table contains the means of all the results, which are referred to the two units now most generally adopted for the measurement of

\* Pogg. *Ann.* Jubelband, p. 585.

† A thesis presented to the Paris Faculty of Sciences.

conductivities, viz. the British-Association unit, or *ohm*, and the Siemens unit.

	Resistance of 1 metre by 1 square millim.		Conductivities, referred to silver.
	Ohm.	Siemens unit.	
Pure silver, annealed.....	0·0154	0·0161	100
Copper, annealed .....	0·0171	0·0179	90
Silver 0·75, annealed .....	0·0193	0·0201	80
Pure gold, annealed .....	0·0217	0·0227	71
Aluminium, annealed .....	0·0309	0·0324	49·7
Magnesium, cold-beaten .....	0·0423	0·0443	36·4
Pure zinc, annealed at 350°.....	0·0565	0·0591	27·5
Pure cadmium, cold-beaten .....	0·0685	0·0716	22·5
Brass, annealed* .....	0·0691	0·0723	22·3
Steel, annealed .....	0·1099	0·1149	14·0
Pure tin .....	0·1161	6·1214	13·3
Aluminium bronze, annealed† ...	0·1189	0·1243	13·0
Iron, annealed .....	0·1216	0·1272	12·7
Palladium, annealed .....	0·1384	0·1447	11·1
Platinum, annealed .....	0·1575	0·1647	9·77
Thallium .....	0·1831	0·1914	8·41
Pure lead .....	0·1985	0·2075	7·76
German silver, annealed ‡.....	0·2654	0·2775	5·80
Pure mercury.....	0·9564	1·0000	1·61

From the third column, which gives the specific conductivities of these metals referred to that of silver, it is seen that the results obtained by the author differ but little from those which have been given by other experimenters.

The diminution undergone by the electric conductivity of the metals with rise of temperature was the essential aim of M. Benoit's researches. This influence of temperature, already remarked by Davy, was studied by Ed. Becquerel, who measured it up to 100°, by Matthiessen, who followed it as far as 200°, and by other physicists. M. Benoit has set himself the task of studying this variation of conductivity within the most extended limits of temperature. The conducting wire on which he operated was wrapped spirally round a cylindrical support of pipeclay, enclosed in a muffle which was immersed in a bath of a volatile liquid heated by aid of a Perrot furnace. The liquid was water, mercury, sulphur, or cadmium, by means of which constant temperatures were obtained of 100°, 360°, 440°, and 860°. Moreover a great number of experiments were made above 360° by aid of a mercury bath, the temperature of which was regulated. These measurements were corrected for the dilatation.

Plates annexed to the memoir give the graphic representation of the results obtained. They show that the increase of the resistance follows a regular course which continues, probably, for all the metals, as for tin, lead, and zinc, as far as their melting-point§.

\* From the wire drawers: copper 64·2, zinc 33·1, lead 0·4, tin 0·4.

† Copper 90, aluminium 10. ‡ Copper 50, nickel 25, zinc 25.

§ Fusion is in general accompanied, as we know from the researches of

This augmentation varies, too, a great deal, from one metal to another. We remark that tin, thallium, cadmium, zinc, lead, are found together towards the upper part: at about  $200^{\circ}$  and  $230^{\circ}$  their resistance has doubled. Still above them are found steel and iron: the resistance of the latter has doubled at  $180^{\circ}$ , quadrupled at  $430^{\circ}$ , at  $860^{\circ}$  is about nine times as great as at zero. Palladium and platinum, on the contrary, approach the axis of the temperatures; it is only in the vicinity of  $400^{\circ}$  and  $450^{\circ}$  that the augmentation has acquired a value equal to that of the primitive resistance. Gold, copper, silver, form an intermediate group. It may therefore be said generally that, the less elevated the fusing-point of a metal, the more rapidly does its conductivity diminish: iron and steel form an exception to this law. In alloys the variation is always less than in the metals which constitute them. In certain of them (German silver for example) it is very slight; and this renders them valuable for the construction of standards and resistance-coils. Approximately, it is in the metals in which the resistance is greatest that its increase, under the influence of heat, is relatively the most rapid. The slight differences of composition which alter so profoundly the absolute resistance, have but a feeble influence on the relative value of its augmentation by rise of temperature.—*Bibliothèque Universelle, Archives des Sciences Phys. et Nat.*, vol. li. pp. 284–287.

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ON THE CONSERVATION AND THE PROPERTIES OF A PLATE OF PALLADIUM SATURATED WITH HYDROGEN BY ELECTROLYSIS. BY R. BÖTTGER\*.

The Author has found that it is only after being heated to redness that a plate of palladium, charged with hydrogen by electrolysis, loses the hydrogen which it held by occlusion. This is readily ascertained by immersing the plate in a solution of ferridecyanide of potassium. In fact, as long as hydrogen is still present at the surface of the palladium, reduction of the ferridecyanide into ferrocyanide is observed, which is easily recognized by means of the properties of the salts of protoxide of iron.

There are also other metals which thus absorb electrolytic hydrogen—as nickel, zinc, and cobalt.

When a plate of palladium is coated with palladium-black, it becomes saturated with hydrogen much more rapidly. If when thus saturated it is wrapped in gun-cotton, the latter explodes at the end of a few seconds, and the plate burns during five or six minutes with a flame of feeble brightness.

A plate of palladium charged with hydrogen and left in the air, loses in time the gas occluded. Placed under water deprived of air, under absolute alcohol, or ether, it loses at first a part of its hydrogen with effervescence, but retains the rest without apparent change.—*Bibliothèque Universelle, Archives des Sciences*, vol. li. p. 185.

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M. L. de la Rive, by a sudden and very great diminution of the conductivity; nevertheless bismuth and antimony form an exception. and become, on the contrary, better conductors on melting.

\* Pogg. Ann. Jubelband, p. 150.

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AND  
JOURNAL OF SCIENCE.

[FOURTH SERIES.]

FEBRUARY 1875.

XI. *Studies on Magnetism.* By E. BOUTY, Professor of  
*Physics at the Lycée of Rheims\*.*

UP to the present time there does not exist a complete theory of the magnet. Notwithstanding the relative simplicity of the phenomena presented by soft iron, one could not expect to explain these apart; and the study of steel magnets is still too little advanced to supply the elements of a satisfactory physical theory.

Such being the situation, I thought that an experimental and close investigation of the phenomena presented by steel magnets (*e. g.* those accompanying their production, union, or separation) would not be devoid of interest. The present is a first attempt in this direction. The questions which form the subject of it, though hitherto very little studied, would yet offer numerous numerical verifications for any accurate theory of magnetism; and this would suffice to render highly important researches of the sort we have undertaken.

Most of the investigations the subject of which has been magnetization by currents refer to soft iron. Lenz and Jacobi†, Joule‡, Müller§, Wiedemann|| especially, and more recently Quintus Icilius¶, Stoletow\*\*, and Rowland†† preoccupied themselves with determining the magnetic moments, temporary or perma-

\* Translated from a copy, communicated by the Author, of a Thesis presented to the Faculty of Sciences, Paris, 1874.

† Pogg. *Ann.* vol. xlvii. (1839). ‡ Phil. Mag. S. 3. vol. ii. (1839).

§ Pogg. *Ann.* vols. lxxix. & lxxxii. (1850, 1851).

|| Ibid. vols. c., cvi. & cxvii. (1857-1862). ¶ Ibid. vol. cxxi. (1864).

\*\* Phil. Mag. January 1873. †† Ibid. August 1873.

*Phil. Mag.* S. 4. Vol. 49. No. 323. Feb. 1875.

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ment, developed by a current of given intensity in a bar placed in the axis of a spiral excited by the current. Several of these physicists treat also, subsidiarily, the same question for steel. As regards the accessory phenomena accompanying magnetization, they are so numerous and varied that they constitute an inexhaustible mine which still, notwithstanding numerous labours, has scarcely been touched. We will cite only those memoirs which have the closest connexion with the subject of the present investigation.

Quetelet\* studied the magnetism produced in a bar of steel by friction with a magnet. He established that the magnetism increases, up to a certain limit, with the number of the frictions, according to precise laws, to which we will return by-and-by. Hermann† and Scholz‡, under the direction of Frankenheim§, proved an analogous augmentation when a bar of steel is brought near the pole (free or covered with paper) of an electromagnet, or when a steel bar is several times introduced into a spiral traversed by a current.

Coulomb||, and afterwards Lamont¶, in their numerous studies on all branches of magnetism, have enriched the science with observations on the influence of the temper of steel upon its moment of saturation, and on the phenomena which accompany the union or separation of superposed magnetized plates. Villari\*\*, and long previously Abria††, made some experiments on the brief duration of the phenomenon of magnetization.

The temporary magnetization of steel, observed for the first time by Musschenbroek and Cëpinus, has been the subject of interesting memoirs by Poggendorff‡‡ and Wiedemann§§.

But the most complete investigation we possess on steel magnets is found in the recent labours of M. Jamin|||. These researches, which it is not our duty to estimate here, open to physicists a path in some sort quite new, and in which we should be happy to have made one step.

## I. METHODS OF MEASUREMENT.

The determination of the magnetic moment of a magnet is most frequently effected by one of the two methods indicated

\* *Ann. de Chim. et de Phys.* Ser. 4. vol. liii.

† *De naturali magnetismo in Chalybem inducendo quanto momento sit tempus.* Vratisl., 1865.

‡ *Quanti sit momenti tempus in magnetismo inducendo, certa quadam fluidi galvanici intensitate adhibita.* Vratisl., 1863.

§ *Pogg. Ann.* vol. cxxiii.

|| *Mémoires de l'Académie*, passim.

¶ *Magnetismus.*

\*\* *Pogg. Ann.* 1873.

†† *Annales de Chimie et de Physique*, Ser. 3. vol. i.

‡‡ *Pogg. Ann.* vol. xlv.

§§ *Galvanismus*, vol. ii.

||| *Comptes Rendus de l'Acad. des Sciences*, 1873-74.

and applied by Coulomb—the torsion method, and that of oscillations. The first is applied especially to bars; the second extends also to small needles, but loses much of its precision when the magnets are of very small dimensions.

Divers physicists, among others Wiedemann\*, have calculated the magnetic moments of a magnetized needle from the deviation produced by it upon a very short magnetized needle furnished with a mirror and movable about a vertical axis. This process is peculiarly suitable when the magnetic moments of one and the same needle variously magnetized are to be compared, provided that the magnetic moments to be compared are not too feeble.

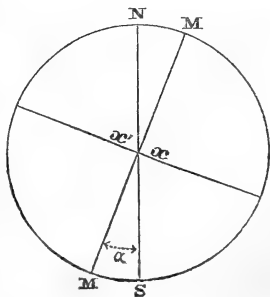
In this case the needle A, whose magnetic moment we wish to compare, is fixed in a horizontal groove, the direction of which is sensibly perpendicular to the magnetic meridian. The distance from the centre of the needle A to the centre of needle B should be sufficiently great relatively to the length of A to avoid a notable alteration of the results by a slight displacement of the poles of A in consequence of a more or less considerable magnetization. The azimuth of the line of the centres of A and B can be chosen arbitrarily; and if the needle A receive the same position in all the experiments, the deviations observed will be proportional to the moment it possesses. If the needle is regular, it may be returned to its groove with its ends reversed, and the mean of the deviations be taken.

I have frequently employed this process of measurement in the study of magnetization by currents; but mostly, as in the study of the breaking of the current, I have had to measure the ratio of the magnetic moments of needles of very small dimensions, and different in length and diameter. I have then made use of a special arrangement, which I will describe in detail.

*Principle of the method.*—Suppose a rigid support, movable about a vertical axis. Fix upon this support (1st) a horizontal needle the magnetic moment M of which is known, (2nd) the needle whose magnetic moment  $x$  we wish to determine. The two needles are placed one above the other in such wise that their axes form a right angle, and at a sufficient distance for their reciprocal action not to alter the distribution of the magnetism in either of them.

The system thus formed takes, under the influence of the earth's magnetism, a determinate position of equilibrium, such that the mag-

Fig. 1.

\* *Galvanismus*.

netic axis of the needle M (fig. 1) makes, with the plane of the magnetic meridian N S, an angle  $\alpha$  determined by the equation

$$x = M \tan \alpha. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the moment  $x$  is sufficiently small in proportion to  $M$ , the angle  $\alpha$  can be determined by Poggendorff's optical method\*. For that purpose the support of the needles carries a small vertical silvered mirror, in which, with the aid of a telescope, the image of a horizontal graduated scale is observed, which is placed beneath and very near the objective, and perpendicular to the optic axis of the telescope.

The moment  $M$  of the directing needle may be made as small as we please. It follows that it is possible by this method to measure the magnetic moment of very small needles, comparable in their dimensions to particles of file-dust. I have been able to effect measurements relative to needles of 2 millims. length and 0.2 millim. diameter.

When we wish only to compare with one another the magnetic moments  $x, x'$  of several minute needles, it is not necessary to know the moment  $M$  of the directing needle; we have, indeed, designating by  $\alpha, \alpha'$  the deviations they produce:—

$$\frac{x'}{x} = \frac{\tan \alpha'}{\tan \alpha};$$

and, on account of the minuteness of the angles  $\alpha$  and  $\alpha'$ ,

$$\frac{x'}{x} = \frac{\tan \alpha'}{\tan \alpha} = \frac{\alpha'}{\alpha} = \frac{\tan 2\alpha'}{\tan 2\alpha} = \frac{n'}{n}, \quad . \quad . \quad . \quad . \quad (2)$$

where  $n$  and  $n'$  are the two readings made upon the scale, the zero of which is supposed to be in the plane of the magnetic meridian.

*Apparatus.*—The support of the needles is merely a small stick, thin and light, of sealing-wax, hard and not readily fusible. The directing needle A B (fig. 2) is attached to the lower extremity of the wax; and a very narrow glass tube T passes through the latter towards its upper part, in such a way that its axis is horizontal and perpendicular to the axis of the directing needle. The system is suspended by a nipper or hook of copper to a single cocoon-thread, and enclosed in a wooden box blackened on the inside, and closed in front by a plane glass. The cocoon-thread passes through an aperture in the top of the box, and is grasped by a brass nipper. And a disk of red copper is placed under and very near the directing needle, the oscillations of which it deadens.

\* “Methode der Spiegelablesung” (Pogg. *Ann.* vol. vii. 1826), employed by Gauss (*Göttingische gelehrte Anz.* 1833, Nos. 205–207), to whom the invention of it is most frequently attributed.



Fig. 2.

The following are the dimensions of one of the apparatus which I have employed:—needle A B, length 6 centims., diameter 0·2 millim.; mirror M, diameter 8 millims.; tube T, length 2 centims., diameter 0·5 millim.; stick, a square prism of 4 millims. in the side, and 5 centims. length.

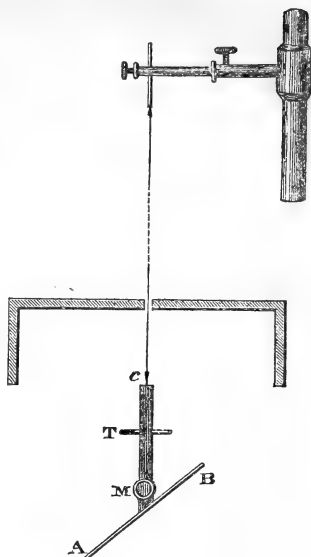
The construction presents no difficulty. The condition most requisite to be realized is, to render the axis of the tube T sensibly perpendicular to the axis of the needle A B. For this a graduated circle of paper is employed; in the centre of the circle the stick of wax is placed with the needle A B already adherent to its lower extremity, and the axis of the needle is made to coincide with the line 0–180°. Then on the upper face of the stick the tube T is placed, with a long and stiff steel wire inside of it; and the axis of the tube is directed so that the eye, placed in the prolongation of the stick, sees the steel wire projected on the line joining 90° and 270°. It is sufficient then to put a lighted match near the base of the tube to slightly melt the wax and fix the tube. Finally another piece of wax, terminated by the nipper c, is fitted on.

The mirror is set perpendicular to A B by placing the image of A B on the prolongation of its direction.

*Placing.*—The placing of the telescope and the scale is done in the usual way\*. The distance chosen, of the mirror from the scale, was equal to 4 metres in most of the experiments, and 7 metres in some of them.

For the regulation of the apparatus, a few drops of wax are added, according to need, before or behind A B, so as to bring the image of the scale into the field. The scale is suspended by a system of strings and counterpoises, so that it can be raised or lowered at will by a simple movement of the hand, without the eye needing to leave the ocular of the telescope. It thus becomes very easy, after a few trials, to bring the mirror M into a rigorously vertical position; and consequently the bar A B, perpendicular to the mirror, is itself horizontal.

\* *Vide the writings of Gauss and Weber, or Verdet, Conférences de physique faites à l'École Normale.*



The optic axis of the telescope will be normal to the mirror when the image of the objective occupies the centre of the field. The other conditions, relative to the scale, may be fulfilled approximately; and we shall see by-and-by how this is accomplished.

It is to be remarked that, when a needle is introduced into the axis of the tube T, the centre of gravity of the suspended system is in general displaced slightly; but it is easy to see that this displacement has no influence on the readings. In fact we can produce the corresponding displacement of the suspended system by the combination of two rotations:—one about an axis perpendicular to the mirror, without influence on the phenomenon of reflection; the second about a horizontal axis parallel to the mirror, the effect of which is to raise or lower the normal to the mirror in a vertical plane—that is, to raise or depress the image of the scale. This perturbing effect is, besides, reduced to its minimum by disposing the mirror parallel to the axis of the tube in which the needles are placed. The rotation about the axis of suspension, produced by the introduction of a magnetized needle, is due solely to the earth's action, as we have above supposed.

*Corrections and Mode of Observation.*—The axis of the tube T is never quite horizontal; but when we confine ourselves to relative measurements (we shall see how absolute measures are reduced to relative ones), it is enough if the axis has always the same inclination. For this the weight of the needles introduced into the tube must be very little in proportion to the total weight of the apparatus.

We have supposed that the vertical planes which contain the axis of the tube and the axis of the directing needle form a right angle. In general they make with each other an angle  $\frac{\pi}{2} - \beta$ : the precise formula which would replace formula (1) on this hypothesis would be

$$x = M \frac{\sin \alpha}{\cos (\alpha + \beta)}, \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

in which, to quantities of the second order relative to  $\beta$ ,

$$x = M \tan \alpha (1 + \beta \tan \alpha). \quad . \quad . \quad . \quad . \quad (3)$$

If the needle be turned in the tube end for end, the angle of the two planes becomes  $\frac{\pi}{2} + \beta$ , and we have,  $\alpha'$  denoting the new deviation,

$$x = M \tan \alpha' (1 - \beta \tan \alpha'); \quad . \quad . \quad . \quad . \quad (4)$$

from which, adding (3) and (4) term to term, and observing

that  $\tan \alpha - \tan \alpha'$  is extremely small, we have, excepting quantities of the second order :—

$$x = M \frac{\tan \alpha + \tan \alpha'}{2} \dots \dots \dots (5)$$

It will therefore be sufficient to take the mean of the two observations to correct the result of the imperfection of the apparatus\*.

Again, in the preceding we have supposed that the magnetic meridian is invariable, which is not rigorously true ; besides, our apparatus realizes a veritable compass of variations ; consequently the error resulting from the variations of the declination is an appreciable quantity in the conditions in which we are placed.

Except the case of abrupt and irregular variations, this cause of error will be eliminated by making a third measurement after restoring the needle to its first position, turning it end for end. If the observations have been made at nearly equal intervals, the mean of the first and third measurements may be taken, and the mean of this and measurement 2 will not be sensibly affected by the variation of the declination. In all cases the equality of Nos. 1 and 3 will be a guarantee of the accuracy of the measurement.

For the purpose of making an observation, the oscillations of the apparatus are first eased by hand, in order to abridge the duration of an experiment. Besides, as soon as the amplitude of the oscillations is sufficiently small, the divisions  $n_1$  and  $n_2$  of the scale, corresponding to the commencement and the end of an oscillation, are noted, and the division  $n_3$ , corresponding to

the end of the following oscillation. The mean,  $N = \frac{\frac{n_1 + n_3}{2} + n_2}{2}$ , is taken several times ; and thus the position of equilibrium is determined with great exactness.

The number  $N$  also has to be corrected when the deviation is rather considerable, in such a manner that the arc cannot be confounded with its tangent. To effect the reduction a Table is employed, giving the values of  $\tan \alpha$  when  $\tan 2\alpha$  is known†. The distance of the scale from the mirror being known approximately, it is easy to draw up a Table giving the reduced values

\* The two readings  $n$  and  $n'$ , corresponding to the deviations  $\alpha$  and  $\alpha'$ , will differ very little from one another, if the scale be exactly perpendicular to the optic axis of the telescope. This condition will be realized by rotating the scale, in a horizontal plane, about its centre until the two readings  $n$  and  $n'$ , obtained with one and the same needle direct and reversed, differ the least possible one from the other.

† See a Table of this sort in Wiedemann's *Galvanismus*, vol. ii. p. 207 (2nd edition).

$N_1$  for a great number of values of  $N$ . For the intermediate values proportional parts are taken.

The masses of iron distributed, in fixed positions, in the laboratory where the operations are carried on, have no influence on the measurements, provided that they are not too near the apparatus; they merely modify the azimuth of equilibrium, which we take for our magnetic meridian.

In short, a space of ten minutes is sufficient for accomplishing a good experiment; and the result of several successive measurements of the same needle furnishes, in general, numbers equal within  $\frac{1}{200}$  of their value. Moreover the operation becomes so simple and convenient with practice, that we prefer to employ this method even in those cases in which the oscillation method would give good results.

*Comparison of several Apparatus, and Absolute Measures.*—One has often to compare several apparatus. This is accomplished by effecting the measurement of the moment of one and the same needle by means of two apparatus which we wish to compare. Another needle, suitably selected (larger, for instance), will permit the comparison of the second apparatus with a third, and so on.

Further, all the relative measures can be converted into absolute measures: for this it is sufficient to determine, by the oscillation method, the magnetic moment of a needle, and afterwards measure it by means of the apparatus which have been compared.

## II. ON MAGNETIZATION BY CURRENTS.

### 1. *On Extra Currents.*

A coil of conducting wires possesses magnetic properties as long as it is traversed by a current. During the time occupied in establishing the current the production of this magnet absorbs a certain quantity of work in addition to that which would be necessary to establish the current in an equal linear resistance. This absorption of work is manifested outside the coil by the inverse extra current.

When the current is interrupted, the destruction of the magnetic property of the coil restores the work absorbed in its production; hence the direct extra current, equal in quantity to the inverse. As experiment shows that the first is shorter in duration than the second, we can affirm that the magnetic property of the coil is lost more quickly than it is produced.

When a coil of conducting wires is furnished with a core of soft iron, the extra currents retain their character, but are much augmented in intensity. This augmentation measures the work absorbed by the magnetization, or restored by the demagnetiza-

tion of the soft iron. The inequality of duration of the extra currents authorizes us to affirm that the demagnetization of soft iron is more rapid than its magnetization\*.

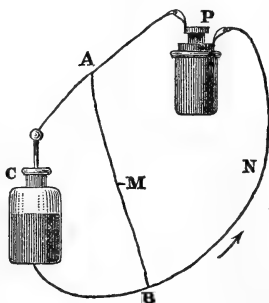
Analogy has led physicists to regard the coil, which gives rise to the extra currents, as the seat of temporary electromotive forces the same in direction as, or contrary in direction to the principal current; but it does not authorize us to identify in all points the interior of a coil with that of an element of a pile and, consequently, to regard the extra currents as having the same effects inside the coil as in the rest of the circuit. We shall see that the extra currents are without effect within the coil from which they emanate.

A condenser C (fig. 3) placed in a voltaic circuit, on a derivation, is, like an induction-coil, the seat of temporary electromotive forces at the time of the opening or closing of the circuit. We will examine only the two following cases.

1st. The condenser C is placed on a derivation without resistance, on which the interruptions are made. The points of bifurcation, A and B, have the same potential when the current passes, since the derivation is destitute of resistance and consequently the condenser is not charged. When the current is interrupted the difference of potential in A and B becomes equal to the electromotive force of the pile P. Thus the condenser discharges itself during the period of the establishment of the current, and becomes charged at the time of the interruption, whence there result in the principal circuit B N P A an inverse and a direct extra current.

2nd. The condenser C is placed on a derivation the resistance of which is sufficiently great for that of the rest of the circuit, including the pile, to be negligible. The interruption is made at N, apart from the derivation. In this case the points of bifurcation are at the same potential when the current is interrupted; but when it is passing, the difference of their potentials is sensibly equal to the electromotive force. The extra currents are

Fig. 3.



\* Villari (Pogg. *Ann.* 1873) has determined directly the time taken by flint, a diamagnetic substance, to gain or lose its magnetic rotatory power, the correlative of its magnetization. He found that the demagnetization is more rapid than the magnetization, and assigns to this latter a duration of 0.0024" (see *Journal de Physique*, vol. ii. p. 422). This is the only experimental determination I know of in regard to the duration of magnetization.

produced in the derivation, and are inverse on the closing, direct on the opening of the circuit.

We should add that, from our present point of view, a very feeble coil is equivalent to a conductor of enormous capacity.

## 2. *On the Magnetization of Steel.*

A steel needle, recently tempered, is transported from infinity into the interior of a spiral animated by a current, and then extracted from the spiral and transported to infinity in the opposite direction. This needle is attracted into the spiral; and during its introduction the work absorbed by the magnetization of the steel is added to the work of the attractive forces developed between the spiral and the needle. These two effects in the same direction produce in the wire outside the coil an induced current opposite in direction to the principal current. When the needle is withdrawn from the coil, the work restored by the loss of the temporary magnetization is added to the negative work of the attractions—whence a direct induced current outside the coil\*.

The considerations unfolded in the preceding article concerning the extra currents apply also to the induced currents. It is probable that these currents are without effect within the coil from which they emanate. In all cases, if the needle is introduced or extracted very slowly, the intensity of the induced currents is very feeble; and in this case, at least, their magnetic effect within the coil may be neglected. We have therefore good ground for admitting that the magnetism carried away by a needle which is passed once to the spiral is due solely to the action of the principal current.

I. The circuit comprises only a pile with a constant current and the coil within which the magnetizing takes place.

(1) If the needle be introduced and extracted slowly, and the permanent magnetic moment which it has carried away be measured, we find that repetition of the passing of the needle augments the residual moment. It tends, through the repetition, towards a limit  $A$ ; and the magnetic moment  $y$ , after  $x$  passages, is sufficiently well represented by the empiric formula

$$y = A - \frac{B}{x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

\* This direct current is equal in quantity to the inverse current; whence this proposition:—The work absorbed by the production of permanent magnetization is equal to the excess of the work of the attractive forces during the extraction of the magnet from the spiral above the work of the same forces during its introduction. The permanent magnetization has therefore a mechanical origin, and derives nothing from the current.

in which  $A-B$  represents the residual magnetic moment after the first passage. The degree of accuracy of the formula will be seen from the following examples.

TABLE I.—Needle 2 millims. in diameter, magnetized by 1 Grove's element.

Number of passages to the spiral.	Magnetic moment.		Difference.
	Observed.	Calculated.	
1	51.46	51.46	0.00
2	54.55	54.62	-0.07
3	55.43	55.68	-0.15
4	56.10	56.20	-0.10
5	55.95	56.51	-0.56
10	56.48	57.15	-0.67
20	57.68	57.47	+0.21
30	57.92	57.57	+0.35
50	57.75	57.68	+0.07
A=57.78, B=6.32.			

TABLE II.—Needle 1.3 millim. in diameter, magnetized by 1 Bunsen element.

Number of passages to the spiral.	Magnetic moment.		Difference.
	Observed.	Calculated.	
1	37.50	37.50	0.00
2	39.37	39.51	-0.14
3	39.99	40.18	-0.19
4	40.47	40.52	-0.05
8	41.09	41.01	+0.08
16	41.52	41.27	+0.25
A=41.52, B=4.02.			

The curious augmentation in question has been already observed by Hermann and Scholz\*. They wrongly confound, in their researches, the effect of a magnetizing spiral and that of a horseshoe magnet, to the poles of which they apply the needle to be magnetized. In the first case, indeed, if the needle is thin enough, it may be regarded as placed in a magnetic field of constant intensity, which it certainly is not in the second; and as it is impossible to place the needle in precisely the same manner in a great number of successive experiments, the law of the increase is masked by a phenomenon of a different kind. These authors

\* Hermann and Scholz, *locis citatis*.

were therefore unable to find an empiric formula fitted to represent the results of their experiments; but, taking only the numbers obtained by means of the magnetizing spiral, we shall see from the following Table that they agree as well as possible with our own empiric formula\*.

TABLE III.

Number of passages.	First needle.		Second needle.		Third needle.	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
1	8.39	8.39	7.07	7.07	8.88	8.88
2	9.34	9.34	8.17	8.17	9.76	9.76
3	9.66	9.66	8.84	8.54	10.08	9.99
4	9.71	9.82	8.73	8.72	10.43	10.24
5	9.90	9.91	9.15	8.83	10.27	10.29
6	.....	.....	.....	.....	10.31	10.31
$\infty$	10.15	10.29	9.32	9.27	11.03	10.64

The augmentation of the magnetic moment by repetition of the passages is independent of the duration of the immersion, as Hermann and Scholz had ascertained; it is essentially connected with the intermission of the action of the current. It must, then, be admitted, since the induced currents themselves are without sensible effect, that the magnetic equilibrium which succeeds the action of the currents modifies the distribution of the magnetism in such wise that a second application of the same force, acting under the same conditions, may add to the total residual magnetism†.

(2) Three other processes may be employed to magnetize a steel needle within a coil:—

*a.* The needle is introduced, the current established, and the needle withdrawn slowly (establishment).

*b.* The needle is introduced slowly, the current passing; the current is interrupted, and the needle withdrawn (interruption).

*c.* The needle is introduced; the current is established, and

\* The authors do not state what is the limit of the errors of experiment in their measuring-process; but it is certain that they exceed the greatest differences between the numbers in the column of the observations and in that of the calculated numbers.

With the exception of the three experiments contained in this Table, the authors confine themselves to the observation of the magnetic moments corresponding to 1, 2, and  $\infty$  passages. The application of the empiric formula gives the third number by means of the two first, with sufficient approximation whenever the magnetization has been obtained by the spiral. In the opposite case the calculated third number is notably less than the number observed. They found that the degree of tempering, the length of the needles, and the duration of the immersions are without influence on the results.

† The fact we are describing should be compared with the known fact



then interrupted; and then the needle is withdrawn (disruptive discharge).

The repetition of each of these processes furnishes an increment of magnetism to the needle; and, provided that all the operations effected are of the same sort and the conditions identical, the results of the experiments are well represented by a hyperbolic formula such as formula (1). The limit  $A$  appears to be the same for the passages and the interruptions, but less for the establishments.

TABLE IV.—Needle 2 millims. in diameter, magnetized by 1 Grove's element.

Number of establishments.	Magnetic moment.		Difference.
	Observed.	Calculated.	
1	50.56	50.56	0.00
2	52.81	52.81	0.00
3	53.50	53.56	-0.06
4	53.83	53.93	-0.10
5	54.25	54.16	+0.09
6	54.18	54.31	-0.13
10	54.75	54.61	+0.14
$A=55.06, B=4.50.$			

After the tenth passage, interruptions having been produced unawares, the moment of the needle suddenly rose to 55.96, and was not carried beyond that limit by 50 establishments. Ten passages with the spiral then raised the magnetic moment to 57.56, and twenty more passages to 57.88.

TABLE V.—Needle 2 millims. in diameter, magnetized by 1 Grove's element.

Number of interruptions.	Magnetic moment.		Difference.
	Observed.	Calculated.	
1	53.15	53.15	0.00
2	55.93	55.93	0.00
32	58.73	58.55	+0.18

that the permanent magnetism produced by a current  $A$  becomes more considerable when the needle, after magnetization, has been submitted to the action of a current  $B$ , feebler and in the opposite direction. If  $B$  is made to tend to 0, the phenomenon still continues; and this is not at all surprising, since partial demagnetization (corresponding to loss of the temporary magnetism) is the consequence of the cessation of the current  $A$ .

Thirty passages to the spiral did not raise much the magnetic moment of this needle\*. The results obtained by the disruptive discharges are less regular than the preceding, although the empiric formula still represents them. The irregularities doubtless proceed from the difficulty of working these discharges in perfectly identical conditions.

The preceding experiments already establish that the extra currents are without magnetic action within the coil which produces them. If it were otherwise, interruption would be a more efficacious process of magnetization than passing the needle to the spiral; now augmentation of the magnetic moment has never been observed when needles magnetized by a great number of passages have been submitted to repeated breakings of the circuit.

II. The circuit comprises, besides the pile, two coils P and Q.

The phenomena observed on account of slow passages are the same as in the case of a single coil; but the effect of the extra currents complicates the phenomena arising from interruption. We will suppose the coil P much more powerful than Q. If the two coils are placed one after the other, two needles *p* and *q*, magnetized, each in the corresponding coil, to the limit relative to the passages, acquire a greater magnetic moment through the interruptions; but the relative increment is much greater in the less powerful coil. Example:—

TABLE VI.—Needles 142 millims. long and 2 millims. in diameter.

Needle <i>p</i> .	Needle <i>q</i> .
First passage..... 17·51	First passage ..... 3·22
Second passage..... 18·21	Second passage ..... 3·63
Twentieth passage.. 18·70	Twentieth passage ... 4·15
21 interruptions ... 18·91	21 interruptions ..... 5·61

The extreme magnetization corresponding to the passages, from the first two observations of each column, would be, according to our empirical formula, 18·61 for *p*, and 4·04 for *q*. The increment of the magnetic moment produced by the interruption is, for *p* 0·21 in absolute value, and about  $\frac{1}{94}$  in relative value; for the needle *q* the values are 1·46 and  $\frac{1}{3}$ .

\* The two preceding experiments were made immediately after those of Table I., with needles almost identical and in the interior of the same spiral. The establishments and interruptions are effected by means of a cup containing mercury, into which the extremities of the conducting wires dipped.

Therefore, conformably to the observations we have previously given, the extra current proceeding from P is sensible in Q, that from Q in P, but the magnetic effect of each is *nil* in the coil from which it emanates.

If the coils P and Q are placed as derivations with respect to one another, the direct extra current of each coil traverses the other in a direction contrary to the current from the pile. In this case experiment shows that the interruptions occasion a diminution of the magnetic moment, and the establishments an augmentation, as might have been foreseen from what precedes.

III. The circuit comprises a coil and a condenser.

This case is realized with a Ruhmkorff coil in the following manner: the condenser C (fig. 4) is fixed in a derivation destitute of resistance, on which the interruptions are practised. The coil B may also be placed in the derivation, and the interruption be produced in a point of the principal circuit (fig. 5).

Fig. 4.

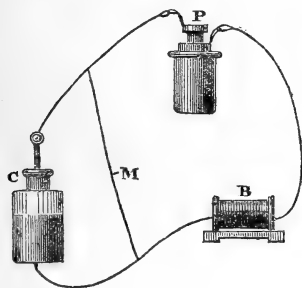
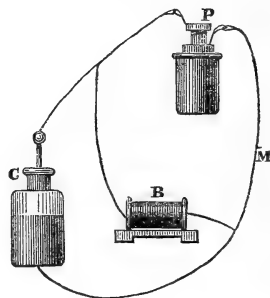


Fig. 5.



In each of these arrangements the condenser forms with the coil a closed circuit apart from the interruption, either directly or by the intermediation of the pile. It would not be the same if the interruption were made in the principal circuit with the arrangement of fig. 4, or in the derivation in the case of fig. 5: these last two arrangements are useless, as experiment has shown; but if one of the former be employed, the rupture of the circuit is observed to produce a diminution of the magnetic moment of the needles magnetized by being passed to the coil.

The effect observed cannot be attributed to the extra currents of the condenser; for these act in a direction contrary to the result obtained. The condenser employed\* behaves, with respect to the production of extra currents, like a coil of negligible power.

\* That of a Ruhmkorff coil, of which the explosion-distance is 3 centims.

But it must be remarked that the intensity of the extra current of the coil is superior to that of the principal current. The direct extra current strongly charges the condenser, which must consequently discharge itself after the extra current has ceased. The coil thus receives, *by reflection*, the extra current which it has produced, and is traversed by it in the opposite direction to that of the principal current. The reflex effect is, for a given condenser, the more intense the more powerful the coil employed; and experiment shows that with a very feeble coil the effect of the interruption vanishes.

IV. *Magnetization by induced currents*.—We have studied only the following case:—

When the circuit includes two coils, the slow introduction of a core of soft iron into one of them, or its extraction, is without effect upon the magnetism of a needle placed in the other coil. But if the core be introduced slowly and withdrawn suddenly, the direct induced current augments the magnetic moment of the needle placed in the second coil. Repetition of the same operation causes the moment of the needle to tend towards a limit, which it rapidly approaches. The formula

$$y = A + B(1 - e^{-\alpha x}), \quad . . . . . (2)$$

in which  $A$ ,  $B$ , and  $\alpha$  are constants, appears very well adapted to represent the magnetic moment  $y$  after  $x$  passages. The following Table permits the appreciation of the degree of accuracy of the formula:—

TABLE VII.

Number of direct induced currents.	Magnetic moment.		Difference.
	Observed.	Calculated.	
0	71.55	71.55	0.00
1	75.30	75.55	−0.25
2	78.55	78.53	+0.03
3	80.50	79.20	+0.70
4	80.80	80.03	+0.77
8	81.05	80.92	+0.13
16	81.05	81.03	+0.02
A = 71.55, B = 9.50, $\log e^{-\alpha} = 1.7626391$ .			

The differences between calculation and observation are a little more considerable in this Table than in the preceding ones; but account must be taken of the difficulty of always withdrawing the soft iron in identically the same manner, in order to produce induced currents of the same intensity. Regard being

had to this consideration, the agreement is satisfactory. On the contrary, hyperbolic formulæ are not at all suitable for the representation of experiments of this sort; they correspond to a much slower increase, sensible even after twenty operations of the same kind, while here the augmentation ceases to be appreciable after seven or eight operations.

Quetelet represents by a formula of the form

$$y = B(1 - e^{\alpha x}) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the magnetic moment acquired by a steel bar magnetized by one, two, . . .  $x$  frictions. This formula represents also, as we have just seen, the increment of the magnetic moment produced in a needle by equal induced currents; it does not suit for that produced by the interruptions of one and the same continuous current, acting on a needle innocent of all anterior magnetization. A complete theory of magnetism should account for this difference.

To avoid the intermissions of the principal current in the preceding experiment, the needle should have been placed in a fixed position in its spiral, and its *total* magnetic moment measured by the method of deviations. The variations observed are related to the permanent magnetism, which may alone be altered by the passage of the induced currents.

We have seen that the induced currents produced by wresting from contact an electromagnet placed in the circuit produce absolutely similar effects.

V. *Effects of piles the current of which is not constant*.—If the current of the pile employed is not rigorously constant, the effect of the polarization of the electrodes modifies profoundly the phenomena. The following results were obtained with a pile containing bichromate of potash, prepared several days previously.

If the circuit comprises, besides the pile, only one coil, into which a needle magnetized by a great number of passages is introduced, the establishment of the current augments the magnetic moment by a quantity more or less considerable, often enormous. The current therefore possesses a much greater intensity at the moment of its closing than it retains a moment afterwards. When the resistance of the spiral is augmented, the polarization is less strong, and consequently the proper effect of the establishment of the current tends to disappear.

With respect to the interruptions, they have no very marked effect upon the needles, at least while the resistance of the coil is not very strong; but in the latter case, if we introduce into the coil a strongly magnetized needle with its south pole to the left of the principal current, we always obtain by the interrup-

tion a diminution of the magnetic moment of the needle. I think that this strange effect must be explained thus:—The direct extra current of the coil, without magnetic effect in its interior, momentarily increases the polarization of the pile, whence a current of very perceptible depolarization in consequence of the interruption; this current partially demagnetizes the needle. We have here, therefore, to do with a reflex effect, analogous to that of the condenser of the Ruhmkorff coil, although incomparably more feeble.

If the circuit contains two coils, P and Q, one very powerful, the other very feeble, the direct extra current of P and the reflex action of the pile succeed each other in Q, and produce a very singular effect. Interruption of the circuit augments greatly the magnetic moment of a needle magnetized in Q by a great number of passages; but the same operation diminishes the magnetic moment of a strongly magnetized needle placed in Q with its south pole to the left of the principal current. This effect is much more pronounced when P contains a core of soft iron. Example:—

	Moment.
Needle magnetized in Q by passages . . . . .	1·16
Interruptions . . . . .	11·10
Needle strongly magnetized . . . . .	36·28
Interruptions . . . . .	35·40

Thus one and the same complex instantaneous current magnetizes needles which were not magnetized, and partially demagnetizes needles which were strongly magnetized. The same thing can be easily reproduced by the alternation of a continuous direct current and a weaker inverse current.

We thus see that, in certain cases, magnetized and non-magnetized steel needles permit us to analyze a complex instantaneous current, and recognize in it a change of sign.

[To be continued.]

XII. *On the Mathematical Theory of Mr. Baillie Hamilton's String-Organ.* By R. H. M. BOSANQUET, *Fellow of St John's College, Oxford*.\*

THE investigation which follows was completed more than a year ago (1873). The endeavour was then made to test the theory by experiment; but difficulties were encountered which, notwithstanding the assistance kindly afforded by Mr. Hamilton, were not got over. The subject has now been brought repeatedly before the public by Mr. Hamilton, who has read

\* Communicated by the Author.

papers before the Physical Society, the Ashmolean Society of Oxford, and the Musical Association; and in view of the interest generally expressed about it, I have thought that an account of the theory, as far as it goes, may be acceptable to the readers of the *Philosophical Magazine*. The two sets of observations given towards the close of these remarks were made by me at Mr. Hamilton's laboratory in November 1874.

It is not my purpose to describe the instrument here; it will be sufficient to point out that it produces continuous tones by means of combinations of strings and harmonium-reeds. There is a separate string to each note, and to some point on each string the extremity of a harmonium-reed is attached. The reed is then set in vibration by wind; and the problem is to determine the forms of vibration of the combination.

The method of the following investigation is substantially that employed at p. 139 of Donkin's '*Acoustics*,' with the extensions necessary for the purposes of the problem.

The instrument may be regarded as a string loaded at the point of attachment to the reed, subject also at the same point to a force tending towards the position of rest, and varying directly as the displacement of the point from that position; this force represents the elasticity of the reed.

Let  $\mu$  be the load at the point of attachment,

$T$  the tension of the string,

$\rho$  mass of unit of length of string,

$\alpha$  elastic force of reed per unit of displacement,

$y$  the displacement,

$l$  the length of the string,

$b$  distance of point of attachment from one end,

$x$  distance of any point from the same end,

$$a^2 = \frac{T}{\rho}.$$

Then the equation of motion of the point of attachment is

$$\mu \frac{d^2 y}{dt^2} = T \Delta \frac{dy}{dx} - \alpha y; \quad . \quad . \quad . \quad . \quad (1)$$

and for the rest of the string

$$\frac{d^2 y}{dt^2} = a^2 \frac{d^2 y}{dx^2}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Assume (see Donkin's '*Acoustics*,' pp. 119, 139)

$$y = \sin m(l-b) \sin mx (A \cos amt + B \sin amt) \quad . \quad . \quad (3)$$

from  $x=0$  to  $x=b$ , and

$$y = \sin mb \sin m(l-x) (A \cos amt + B \sin amt) \quad . \quad . \quad (4)$$

from  $x=b$  to  $x=l$ .

Either (3) or (4) gives for  $x=b$

$$\frac{d^2y}{dt^2} = -a^2m^2 \sin mb \sin m(l-b)(A \cos amt + B \sin amt).$$

And taking the difference of the values of  $\frac{dy}{dx}$  given by the two equations when  $x=b$ , we have

$$\Delta \frac{dy}{dx} = -m \sin ml (A \cos amt + B \sin amt).$$

Hence, in order to satisfy (1), we must have

$$\begin{aligned} \mu a^2 m^2 \sin mb \sin m(l-b) &= Tm \sin ml + \alpha \sin m(l-b) \sin mb, \\ \text{or} \quad (\mu a^2 m^2 - \alpha) \sin mb \sin m(l-b) &= Tm \sin ml. \end{aligned} \quad (5)$$

This equation determines  $m$ , while  $A$  and  $B$  remain arbitrary unless the initial circumstances of the motion are given.

Put  $\mu = \rho \lambda_0$ , where  $\lambda_0$  is the length of the string, the weight of which is equal to the load.

Put  $\frac{\alpha}{\mu} = a^2 \nu^2$ , so that  $a\nu = \frac{2\pi}{t}$ , where  $t$  is the periodic time of the reed with the load vibrating alone. This combination will be referred to as "reed alone."

Then  $a = a^2 \nu^2 \cdot \rho \lambda_0$ , and equation (5) becomes

$$(m^2 - \nu^2) \lambda_0 \sin mb \sin m(l-b) = m \sin ml. \quad (6)$$

Now  $a$  is the velocity of transmission along the string. Let  $\tau$  be the periodic time of the vibration actually sounded,  $\lambda$  the corresponding complete wave-length on the string (*i. e.*  $\lambda =$  twice the length of a single segment).

Then, from the form of (3), (4),

$$m = \frac{2\pi}{a\tau} = \frac{2\pi}{\lambda}.$$

Similarly, if  $\Lambda$  be the wave-length on the string of the note of the reed alone,

$$\nu = \frac{2\pi}{\Lambda}.$$

This transformation is convenient; but it must be remembered that the notes denoted by  $\lambda$  and  $\Lambda$  are those which would be given by single segments of lengths  $\frac{\lambda}{2}$ ,  $\frac{\Lambda}{2}$  respectively. Making the substitutions above indicated, the equation (6) becomes

$$2\pi(\Lambda^2 - \lambda^2) \lambda_0 \sin \frac{2\pi b}{\lambda} \sin \frac{2\pi(l-b)}{\lambda} = \Lambda^2 \lambda \sin \frac{2\pi l}{\lambda}, \quad (7)$$



which is the complete equation of the problem. The calculation of  $\lambda$  in the general case presents great difficulty; and before a comparison of theory with experiment could be effected, it would be necessary to measure the length, weight, and tension of the string, the distance of the point of attachment from one end, the note of the reed alone ( $\Lambda$ ), and the load ( $\lambda_0$ ). The last element cannot be directly ascertained by any means with which I am acquainted.

The following are particular cases in which equation (7) is satisfied.

I. If  $n, r$  are integers and  $\frac{n\lambda}{2} = b$  or  $=l-b$ , the left-hand side of (7) vanishes; equating the right-hand side to zero, we must have also  $\frac{r\lambda}{2} = l$ , or  $\frac{\lambda}{2} = \frac{l}{r}$ .

Now  $\frac{\lambda}{2}$  is the length of a segment of the string which would give the note actually sounded. Hence in this case the note sounded is a harmonic of the string alone. And the case arises when the point of attachment is a node.

It is obviously true that the string can vibrate in one of its ordinary harmonics if the point of attachment remains at rest; for in this case neither the load nor the elastic force of the reed comes into play. But the case is not a solution of the problem.

II. Again, if  $\Lambda = \lambda$ , or the note sounded be that of the reed alone, the right-hand side of (7) is to be equated to zero, and the note sounded is a harmonic of the string alone, as before. The case is that in which the reed and string would, if independent, vibrate simultaneously. For suppose the attachment severed; the reed will go on speaking its own note and the string its harmonic; and as these are the same note, the motion will go on as if the attachment continued to subsist. This is obviously a possible solution of the problem.

III. If  $\lambda_0$  be indefinitely diminished, we have ultimately the right-hand member of (7) = 0, as before, and the string can sound any of its ordinary harmonics.

This is the case in which the effect of the peculiar arrangement of the reed is insufficient to modify sensibly the normal properties of the string. It is possible that this case may be realized by the employment of a thick and heavy metallic wire.

IV. On the assumption of certain relations between the elements, the formula (7) reduces in complexity. The simplest assumption that can be made is, that the point of attachment is at the middle of the string. According to experiment no discontinuity in the nature of the results arises at this position; con-

sequently it may be expected, from the symmetry, that minute exactness of the position is not of special importance. Putting, then,  $b = l - b = \frac{l}{2}$ , (7) reduces to

$$\pi(\Lambda^2 - \lambda^2)\lambda_0 \tan \frac{\pi l}{\lambda} = \lambda \Lambda^2, \quad . . . . (8)$$

which gives an infinite number of values of  $\lambda$  when  $\Lambda, \lambda_0$  are assigned.

I now assume  $\Lambda = l$  (the reed the octave of the string), and  $\lambda_0 = \frac{l}{4\pi}$ , as a pair of values such as may easily occur, and convenient for calculation, for the sake of seeing the general nature of the results to be expected.

The equation (8) can then be put in the form

$$\tan \pi \frac{l}{\lambda} = \frac{4 \frac{l}{\lambda}}{\left(\frac{l}{\lambda}\right)^2 - 1}.$$

The numbers placed under the head  $\frac{l}{\lambda}$ , in the Table which follows, are approximate values of the first five roots of the above equation. Proceeding further, we should find a root lying between every consecutive pair of integers.

The second column contains the values of the ratios  $\frac{l}{\lambda}$  reduced to equal-temperament semitones; it gives the pitch of the note sounded with reference to the octave of the string.

The third column gives the pitch of the note sounded with reference to the lowest note of the combination, both in equal-temperament semitones and by description.

$\frac{l}{\lambda}$	Pitch, in equal temperament semitones, referred to $\frac{l}{2}$	Pitch, referred to lowest note of combination.	
		Equal-temperament semitones.	Description.
·5868	—9·230		
1·441	+6·326	15·556	Flat major tenth.
2·357	16·132	25·362	Sharp minor sixteenth.
3·295	20·646	29·876	Flat two octaves and tritone.
4·25	25·052	34·282	Sharp two octaves and minor seventh.

Although it has not been possible to get a complete determination of the elements of any experiment, yet the following

observed successions of overtones may not be devoid of interest. There are four notes of the arrangement which I shall call I., and three notes of II. The pitch in semitones is appended for comparison. In both cases the point of attachment was nearly, though not exactly, in the middle of the string.

I.		
No. of segments.	Note observed.	Pitch of overtone, in semitones.
1 .....	A	
3 .....	$b_0$ .....	14
5 .....	$a_1$ .....	23
7 .....	$d_2-e_2$ .....	29.5
II.		
1 .....	G	
3 .....	$b_0$ .....	16
5 .....	$a_1$ .....	25

Comparing these numbers with the overtones indicated in column 3 of the calculated Table, it will be seen that they follow, as far as they go, the general course indicated by theory in the hypothetical case assumed; and it may be inferred that this case furnishes a rough representation of the circumstances of the two experiments examined.

The above results are the only experimental ones which I know of.

The calculation of the length of the middle segment in the hypothetical case follows easily from the numbers in column 1 of the calculated Table. The fundamental, of course, has for its segment the whole string. In the other cases, expressing  $l$  in terms of  $\frac{\lambda}{2}$ , which is the length of each segment except the middle one, we get the middle segment at once, since we know the actual number of segments. (It is hardly necessary to remark that the numbers of segments in the successive overtones are the odd integers, by the symmetry.)

$l =$	Number of segments.	Ratio of middle segment to any other segment.
$2.882 \cdot \frac{\lambda}{2}$ .....	3 .....	.882
$4.714 \cdot \frac{\lambda}{2}$ .....	5 .....	.714
$6.590 \cdot \frac{\lambda}{2}$ .....	7 .....	.590
$8.50 \cdot \frac{\lambda}{2}$ .....	9 .....	.50

So that, as the pitch of the note sounded rises, the reed diminishes more and more the segment to which it is attached, as compared with the others. Of course this remark is confined for the present to cases resembling the hypothetical case.

The note employed may be either the fundamental or any one of the overtones. As these are in general all inharmonious to each other, only one can be used at a time. But it is probable that, in particular cases, some two or more may become harmonious; and they would then be capable of combining in a true periodic motion.

XIII. *Carbon and Hydrocarbon in the Modern Spectroscope.* By W. MARSHALL WATTS, D.Sc., *Physical-Science Master in the Giggleswick Grammar School*.\*

IN the January Number of the Philosophical Magazine appears a paper with the above title by Professor Piazzzi Smyth, which calls for a few words from me by way of explanation.

1. Professor Smyth inquires "why, since for cometary work the reference-spectrum should be of feeble intensity, I do not examine it in that shape, viz. as given by the blue base of the flame of a small alcohol lamp, or the all but vanishing globule of flame when a common gas-light is on the point of going out from inanition?" The answer is simple, that with a spectroscope of six prisms the loss of light is so great that in the spectrum of a blowpipe-flame there would not be more than one line (5165·5) bright enough to be measured, and it was my object to employ as large a dispersive power as possible in order to secure as great accuracy in the determinations as I could.

The same reason explains why, "although the spectrum consists notably and notoriously of *five* bands, viz. the orange, citron, green, blue, and violet," I only give measurements for three of the bands: the orange and violet bands were not bright enough to be measured accurately.

2. An equally simple explanation solves the "strange problem" why the lines 5165·5 and 5585·5 are the best-determined.

5165·5 happens to fall close to the magnesium-line *b*, whose wave-length we know with great accuracy from the labours of Ångström.

5585·5 happens to be exactly coincident with an iron line in the solar spectrum. The first band of the citron group, although brighter than the second, does not fall near to any marked line in the solar spectrum which could be used as a reference-line; and its determination is therefore not quite so exact.

\* Communicated by the Author.

3. *Chemical Parentage of the Spectrum under discussion.*—I freely admit the force of Professor Piazzzi Smyth's remarks on the difficulty of volatilizing carbon; but that does not appear to me to affect the experimental evidence for my assertion that "this spectrum is the spectrum of carbon, and not of a hydrocarbon or any other compound of carbon." That evidence is very simple; this spectrum can be obtained alike from compounds of carbon with hydrogen, with nitrogen, with oxygen, with sulphur, and with chlorine.

Whether or not the spectrum is produced by the *vapour* of carbon is another question; but if this spectrum is, as Professor Piazzzi Smyth asserts, that of a hydrocarbon, will Professor Piazzzi Smyth explain how it is possible to obtain it from cyanogen, a compound of carbon and nitrogen, when no hydrogen is present? I have just repeated the experiment with cyanogen for perhaps the fiftieth time. Dry mercuric cyanide was heated in a test-tube, and the gas evolved was dried by passing through a tube containing phosphoric anhydride; it then passed through a tube provided with platinum wires, the end of which dipped below warm and dry mercury. On passing the discharge from an induction-coil between the platinum wires a spark was obtained which gave the spectrum in question brilliantly, the gas being decomposed and carbon being deposited.

Professor Piazzzi Smyth says that in May 1871, in a paper sent to the Royal Astronomical Society, he "gave such extracts from the authorities on either side as showed that the spectroscopists declaring for pure carbon, in opposition to those pronouncing for carbohydrogen, were blundering little less than the perpetual-motion men of last century." Permit me to quote from a paper communicated by myself to the *Journal of Science* for *January* 1871:—

"At first sight it would appear that carbon is an element unlikely to yield a discontinuous spectrum, inasmuch as it is not known in the gaseous condition; and that if we obtain discontinuous spectra from carbon compounds, they must be due to some compound of carbon. Thus the bright blue lines observed by Swan (1856) in the spectrum of the Bunsen-flame might be supposed to be more probably due to carbonic oxide or carbonic acid than to carbon itself. But we find that these same lines occur not only in the spectrum of the flame, but also in the spectra obtained by passing the electric spark either through carbonic oxide, or olefiant gas, or cyanogen, and the lines thus found to be common to compounds of carbon with different elements must of course be due to carbon itself. Whether they are really produced by carbon in the gaseous state is a question which cannot yet be certainly decided. If the carbon is in the solid

state, we shall then have an exception to the law that incandescent solids give continuous spectra, of which we have only one other example, viz. the spectrum of bright lines obtained by Bahr and Bunsen from glowing erbia. In the case of erbia it is not impossible that the bright lines are really produced by a gas (Huggins and Reynolds, Proc. Roy. Soc. June 16, 1870); and it is by no means improbable that, when a hydrocarbon is burned it is first of all decomposed into its elements, which then combine with oxygen. If this be so, the carbon may exist for the moment in the gaseous state."

The difference to which Professor Piazzzi Smyth calls attention between the spectra of compounds and elements (the difference, namely, between Plücker's "spectra of the first order" and "spectra of the second order") is important. It is perfectly true that the spectrum of carbon is a spectrum of the first order, and would, from that evidence, be inferred to be the spectrum of a compound. If, however, this spectrum be caused by a compound, it can only be a compound of *carbon with carbon*.

XIV. *Note on the Spectrum of Carbon.* By Dr. ATTFIELD, Professor of Practical Chemistry to the Pharmaceutical Society of Great Britain.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

**I**N chemistry, when compounds of an element with dissimilar radicals yield similar reactions with a reagent, the reactions are held to be evidence of the presence of the element, even though that element in its free state be a massive metal and those compounds be liquid or even vaporous or gaseous. At least, to the question "who gainsays the deduction?" the answer is, "at present, no one."

In 1862 I showed that gaseous or vaporous compounds of carbon with dissimilar radicals, when ignited by the aid of the chemical force in flames, or by the electric force in tubes, or in certain cases by either force, yielded identical spectra; and therefrom I inferred that the spectrum was that of carbon, though I could not say whether the carbon was free or combined in the gases and vapours. And who gainsays the deduction? Mr. Piazzzi Smyth, Astronomer Royal for Scotland, in the current Number of the Philosophical Magazine (January 1875).

Mr. Piazzzi Smyth regards my deduction as a delusion, a blunder, an egregious error, a myth, a mistake patronized, he says, by the Royal Society through secret committees, which he designates accursed things, acting occasionally "as very dragons to keep out any salutary doubt expressed on a *favoured* topic."

These are strong terms, especially when penned by an Astronomer Royal, and with the deliberation involved in the circumstances of serial publication. Very strong experimental evidence obtained by himself would surely scarcely justify an Astronomer Royal in the employment of such terms. Yet (will it be believed?) not a tittle of such evidence is forthcoming. Nay, the spectrum which I stated to be that of carbon, a statement confirmed over and over again by eminent chemists and physicists (Plücker, Morren, Marshall Watts), Mr. Piazzzi Smyth asserts is not only not that of carbon, but solely that of a hydrocarbon—again an assertion unsupported by any experimental evidence whatever. It is true that Mr. Smyth quotes Lielegg and Crookes against me. But Lielegg supports me, and Crookes is cited because of an editorial footnote in the ‘Chemical News’ appended to a notice of Morren’s paper, asking experimentalists what they meant by the “vapour of carbon” existing in a flame. As for Lielegg, I will quote without comment the last sentence but one of his paper (Eng. trans. in *Phil. Mag.* March 1869, p. 216:—“Therefore tubes filled with combinations of carbon and hydrogen show the lines of carbon and those of hydrogen; tubes filled with carbonic oxide or carbonic acid gas show those of carbon and oxygen, giving, in fact, a spectrum of carbon, because the extremely small pressure and the high temperature co-operate in reducing the carbon to a gaseous condition.” Plücker, who, with Faraday, General Sabine, and Geissler, spent two or three hours with me at the Royal Institution minutely examining my spectra—Plücker afterwards writes, on Nov. 12, 1862: “Je suis d’accord avec vous sur l’existence du spectre de la vapeur de carbone.” Morren says, on page 6 of the paper already mentioned, “Je me mis donc au travail avec la pensée préconçue de combattre l’assertion émise par le savant anglais; mais il résulte, au contraire, des expériences auxquelles je me suis livré, que M. Attfield a raison, et que c’est bien la vapeur du carbone qui donne le spectre indiqué plus haut.”

I might just refer to some minor statements made by Mr. Piazzzi Smyth. He says, in a paper to which he draws attention as not having been accepted, as he desired, by the Royal Astronomical Society, but afterwards printed in the ‘Observations’ of his own observatory, that the question put by Crookes was never answered. I answered it at once, and the reply was inserted in the ‘Chemical News’ a fortnight after the question was asked. I did not work “in a rich London laboratory.” With ordinary induction-coils, borrowed, the one from a captain in the army, the other from Mr. Gassiot; with a spectroscope which Dr. Frankland would scarcely now own; with tubes and apparatus made by my own hands, and made, I believe chemically clean; and by the aid of well-fitting shutters in an ill-fur-

nished room—under these conditions only did I carry out my research on the spectrum of carbon. The absence of Plates and measurements in my paper is not “. . . explained (in a memoir *crowned* by being printed in the Philosophical Transactions of the Royal Society of London) by its one chief burden (*viz.* putting pure carbon vapour for hydrocarbon) having been grateful to the then already formed prejudices of the secret committee who passed it,” but by the fact stated in my paper, that Professor Swan had already measured and recorded, confessedly with great accuracy, the position of the lines of the spectrum (observed by him in hydrocarbon flames\*).

Spectral analysis brings to light marvellously minute traces of matter, traces difficult to remove even from the surfaces of apparatus, and still more difficult to extract from large volumes of other matter. Have I overlooked traces of hydrocarbons in some of my flames and tubes? Scarcely; for I adopted all precautions known to chemists to obtain chemical purity and cleanliness. Again, other chemists, armed with prejudice against my conclusions, have ended by confirming those conclusions. Still here perhaps is room for sound original investigation; something new could hardly fail to be discovered by eyes trained to observe. Is it too much to expect that a gentleman occupying so high a position as Mr. Piazzì Smyth will either support his statements by such sound evidence or withdraw them altogether†?

JOHN ATTFIELD.

## XV. On the General Theory of Duplex Telegraphy.

By LOUIS SCHWENDLER‡.

[Continued from vol. xlviii. p. 138.]

THE first part of this investigation concluded by giving (Phil. Mag. vol. xlviii. p. 138) the best relations between

\* Had so good an observer as Swan worked, instead of the writer, in 1862, with the light just then shed on spectroscopy, I am sure he would have looked for the spectrum in flames not containing hydrogen, and would thus have discovered what I discovered, the spectrum of carbon.—J. A.

† The tone of Mr. Piazzì Smyth's communication renders desirable on my part an expression of regret that my duties in the department of chemistry to which I was appointed within a month of the publication of my research on the spectrum of carbon, have quite prevented me from carrying on similar researches. That regret is much tempered, however, by my belief that such work would have been done far less efficiently by me than by men like Plücker, Morren, Lielegg, Troost and Hautefeuille, and Marshall Watts. I am obliged to add that nevertheless my labours, from the promotion of original investigation in other directions, have neither been few nor unsuccessful. This is the only notice I can take of the personalities in Mr. Piazzì Smyth's paper.—J. A.

‡ From the Journal of the Asiatic Society of Bengal, vol. xliii. part 2, 1874 (read on the 4th of February, 1874). Communicated by the Author.



the resistances of the different branches of the bridge arrangement—under the limiting supposition, however, that the line used for duplex working was perfect in insulation, or, more generally, that the real conduction-resistance of the line could be neglected against the resistance of the resultant fault\*.

It now remains, therefore, to investigate if the simple relations given are generally true; or if not, what they become in case the line has an appreciable leakage. In fact this is clearly the case of practical importance; since all overland lines, especially long ones, even if constructed on the best known principles, will always have a very considerable leakage; *i. e.* the resistance of the resultant fault ( $i$ ) will generally be by no means very large in proportion to the real conduction-resistance ( $L$ ) of the line.

In order to obtain the best general solution of the problem, we must conduct the investigation with great caution; that is, we must be careful not to introduce beforehand any relation between the different variables, however convenient, that is not necessarily a consequence of the paramount condition to be fulfilled for duplex telegraphy, i. e. *regularity of signals*.

Thus it will be seen that the present general investigation must be conducted somewhat differently from the special one given in the First Part.

It must, however, be understood from the beginning that, whatever the best relations may be which should exist between the different resistances of the bridge method when used on an imperfect line, these relations must revert to the special one given before if we put  $i = \infty$ ; and this fact affords a certain check upon the correctness of the new relations to be found.

*General solution of the first problem for the Bridge Method.*

The annexed diagram (p. 110) represents the general case; and to it therefore I shall refer in the present paper.

The general mathematical question which is to be solved for duplex telegraphy has been stated as follows:—

REGULARITY OF SIGNALS.—D and S are two functions which must be rigidly equal to zero when no variation in the system occurs.—and which for any given variation in the system must be as small as possible, and approximate rapidly towards zero as the variation in the system becomes smaller and smaller.

Further, these two functions D and S were expressed, say for station I., as follows:—

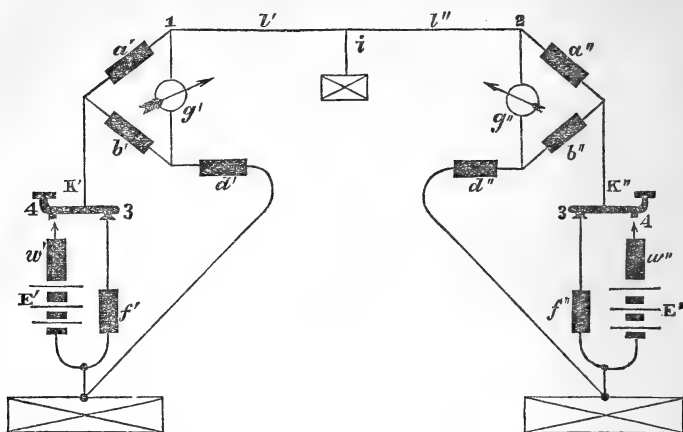
$$D' = \frac{E' N''}{E'' N'} \frac{1}{\mu'} \frac{\Delta'}{m'' \psi'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (III').$$

\* For a definition of the terms "resultant fault," "real conduction," "measured conduction," "real insulation," "measured insulation," &c., which will be of frequent occurrence in this paper, see my 'Testing Instructions,' Part II. Section I.

and

$$S' = E'' \frac{m''}{N''} \mu' \psi' - \frac{E' b'}{n'} + \sigma' \phi' \dots \dots \dots (IV').$$

These two expressions are quite general; *i. e.* they do not as yet contain any restrictive conditions (beyond those involved by



K, telegraph-key of peculiar construction, to be described hereafter.

*g*, the receiving-instrument connected up in that branch of the bridge which, when measuring resistances, would contain the galvanometer.

*a*, *b*, and *d* are the branches of the bridge.

*f*, the resistance between the rest-contact of the key and earth.

*w*, an additional resistance to be inserted in the battery-branch, for reasons to be given further on.

*i*, the resistance of the resultant fault ("real absolute insulation" of the line) acting at a distance *l'* from station I. and at a distance *l''* from station II. (both *l'* and *l''* expressed in resistances so that *l' + l'' = l* equal the "real conductor resistance" of the line).

the mode of arrangement of the system of conductors) between the different variables; and the signification of the abbreviated terms can be found from the First Part\*.

\* For convenience of reference, I shall give here all the terms of which use will be made hereafter.

$$n = b(a + d + g + f) + (a + g)(f + d).$$

$$m = b(g + d) + d(a + g).$$

$$k = b(a + f) + a(f + d),$$

$$\psi = \frac{k}{n}.$$

$$\rho = \frac{\alpha}{n},$$

$$\alpha = b(g + d)(a + f) + ag(d + f) + fd(a + g).$$

These expressions have been obtained by the application of Kirchhoff's rules to the bridge arrangement as represented in the diagram; and they are quite general, as no other relations beyond those represented by the diagram have been introduced as yet.

Now the first relation that we shall introduce is

$$w = \beta = f$$

for both stations, which may be called most appropriately "*the key equation.*"

The introduction of this relation at the outset is quite justified; for say that  $S' = D' = 0$  is rigidly fulfilled in station I. when station I. is sending and the key in station II. is at rest, and suppose the electromotive force in station II. equals 0 (the electromotive force of all elements annulled and only their resistance  $\beta''$  left), then, moving the key in station II. from its rest contact to its working contact, the regularity condition  $S' = D' = 0$  would be (*i.e.* balance in station I.) at once disturbed if  $w'' + \beta'' > f''$  during the motion of the key, even if no variation in the line took place. Thus it is paramount to have  $w + \beta = f$  for each station during the movement of the key\*.

But if, for instance, in station I.

$$w' + \beta' = f',$$

it follows that

$$\phi' = \psi' \dagger.$$

Hence, substituting its value for  $\sigma'$  and reducing, we get more simply

$$S' = \frac{E'm'}{N'} \psi' - \frac{E'b'}{n'}; \quad . \quad . \quad . \quad . \quad . \quad (IV').$$

but as

$$\frac{m'}{N'} = \frac{b'}{k' - \frac{\Delta'n'}{m'}}$$

\* To fulfil the key equation most exactly during the movement of the key, I have constructed a key (constant-resistance key) based on the following principle. During the first movement of the key (up or down stroke) a force is stored up in a spring before the contacts are changed, which force finally causes the change in these contacts; for this reason the two principal contacts of the key coexist only for an almost infinitesimal time, the length of which is moreover independent of the signalling speed. Thus for this key  $w + f = \beta$  is fulfilled in all positions except one, when it is  $\frac{w + \beta}{2}$ , but for such a short time that the error cannot have any disturbing influence whatever.

†  $\psi'$  is the proportion of the total current arriving at point 1 (diagram), which passes off through the instrument  $g'$  when the key of station I. is at rest. Then  $\psi'$ , being a  $r$  function of  $a', b', d', g'$ , is also a function of  $f'$ ;  $\phi'$  is the proportion of the total current arriving at point 1 (diagram), which passes through the instrument  $g'$  when the key of station I. is sending; thus, besides being a function of  $a', b', d', g'$ , it is a function of  $w' + \beta'$  instead of  $f'$ ; and as  $\phi'$  and  $\psi'$  are otherwise quite similar functions, they become identical if we make  $f' = w' + \beta'$ .

and

$$\psi = \frac{k'}{n'}$$

we have

$$S' = \frac{E'b'}{n'} \left\{ \frac{1}{1 - \frac{\Delta'}{m'\psi'}} \right\}. \quad \dots \quad (IV').$$

Therefore  $S'$  approximates most rapidly\* towards zero if  $\frac{\Delta'}{m'\psi'}$  does ; or we have

$$\theta' = \frac{\Delta'}{m'\psi'},$$

which should be as small as the circumstances will allow of.

Now that  $D'$  approximates also rapidly towards zero by making

$$\theta' = \frac{\Delta'}{m'\psi'}$$

as small as possible can be proved as follows :—

By definition we have

$$D' = \frac{p'}{P'}.$$

Further, as  $\phi' = \psi'$  (on account of the key equation), we have

$$p' = S' \text{ invariably,}$$

$$\therefore D' = \frac{S'}{P'}.$$

Thus  $D'$  for any given  $P'$  approximates towards zero at the same rate as  $S'$  does, *i. e.* the smaller  $\theta'$  becomes.

Therefore the whole problem is actually most generally solved by making

$$\theta = \frac{\Delta}{m\psi}$$

as small as possible for both stations.

Now for station I., if balance in the  $g'$  branch for the outgoing current be established, we have

$$a'd' - b'c' = 0,$$

where  $c'$  is the “*measured circuit*” from station I.; and supposing that all variations in the system are chiefly due to variations

\*  $\frac{E'b'}{n'}$  can never become zero, but should, on the contrary, be as large as possible; and therefore  $S'$  can only approximate towards zero by  $\frac{\Delta'}{m'\psi'}$  becoming as small as possible.

in the line resistance\*, we have at once

$$-b'\delta c' = \Delta'.$$

$\delta c'$ , the total variation of the line resistance, may be either positive or negative; and supposing that  $\delta c'$  contains its sign, we have

$$\theta' = \frac{\delta c'}{\frac{m'\psi'}{b}},$$

to be made as small as possible.

Now in case of the line being perfect ( $i = \infty$ ),  $\delta c' = \delta L$  (a constant with respect to the different resistances of each arrangement, as was the case in the first solution). At present, however,  $\delta c'$  is a function of the resistances of the two arrangements, which function must be first determined before we can decide what general condition makes  $\theta'$  as small as possible.

We have

$$c' = l' + \frac{i(l'' + \rho'')}{i + l'' + \rho''},$$

$\rho''$  being the complete resistance of station II.

Put

$$l' = x$$

and

$$l' + l'' = L,$$

$$\therefore c' = x + \frac{i(L - x + \rho'')}{i + L - x + \rho''}.$$

Now  $c'$  may vary from three essentially different causes: namely,

1.  $x$  varies, or the position of the resultant fault alters;
2.  $i$  varies, or the resistance of the resultant fault alters;
3.  $L$  varies, or the real conduction of the line alters, as may happen by an increase or decrease of the temperature along the whole length of the line, or by the occurrence of a partial discontinuity (imperfect joints, loose shackles, &c.).

These three causes may act separately or conjointly; and their total effect we can approximately get by taking the *total* differen-

\* The variations in  $c'$  may be due to variations in the line, or to variations in the duplex arrangements. In the latter case they may be due either to an alteration of temperature in the station; and then the effect can be only small—or to an accident (wire or connexion breaking); and then the influence will become so great that nothing short of actual repairs could help. Thus practically the problem has only to be solved for variations in the line.

tial of  $c'$  with respect to  $x$ ,  $i$ , and  $L$ ;

$$\therefore dc' = \frac{dc'}{dx} dx + \frac{dc'}{di} di + \frac{dc'}{dL} dL,$$

or

$$\delta c' = \frac{dc'}{dx} \delta x + \frac{dc'}{di} \delta i + \frac{dc'}{dL} \delta L \text{ approximately;}$$

which expression is perfectly true, however, for small variations  $\delta x$ ,  $\delta i$ , and  $\delta L$ .

Now\*

$$\frac{m'\psi'}{b'} = \frac{N'}{n'} + \delta c' = \rho' + c' + \delta c',$$

$$\therefore \theta' = \frac{\frac{dc'}{dx} \delta x + \frac{dc'}{di} \delta i + \frac{dc'}{dL} \delta L}{\rho' + c' + \delta c'}.$$

But as  $\delta x$ ,  $\delta i$ , and  $\delta L$  are very small, and as neither  $\frac{dc'}{dx}$ ,  $\frac{dc'}{di}$ ,

\*

$$\frac{m'}{N'} = \frac{b'}{K' - \Delta' \frac{n'}{m'}},$$

$$\therefore \frac{N'}{m'} = \frac{K'}{b'} - \frac{\Delta'}{b'} \cdot \frac{n'}{m'},$$

or

$$\frac{K'}{b'} = \frac{N'}{m'} + \frac{\Delta'}{b'} \cdot \frac{n'}{m'};$$

but

$$\Delta' = b' \delta c',$$

$$\therefore \frac{K'}{b'} = \frac{N'}{m'} + \delta c' \frac{n'}{m'}.$$

Now

$$\frac{m'\psi'}{b'} = \frac{K'}{b'} \cdot \frac{m'}{n'}.$$

Substituting for  $\frac{K'}{b'}$  its value, we get

$$\frac{m'\psi'}{b'} = \frac{N'}{n'} + \delta c';$$

but

$$N' = c'n' + \alpha',$$

$$\therefore \frac{N'}{n'} = c' + \frac{\alpha'}{n'};$$

but

$$\frac{\alpha'}{n'} = \rho',$$

$$\therefore \frac{N'}{n'} = c' + \rho',$$

or

$$\frac{m'\psi'}{b'} = c' + \rho' + \delta c'.$$



This result might, of course, have been anticipated from the special solution, since equation (VIII.) gives only a relation between the branches, quite independent of  $i$ . It remains now to determine the magnitude of one of the branches; and to this end we have to consider the magnetic moments of the receiving instruments.

*Maxima Magnetic Moments.*—By definition we have

$$S = P - Q$$

for both stations; and as it has been proved before quite generally that  $S=0$  if  $\Delta=0$  (*i. e.* if rigid balance in the station for the outgoing current be established), we know at once that at or near balance the currents which in one and the same station produce single and duplex signals must be identical—and need therefore express the magnetic moment in each station for *one* current only, by presupposing balance in both the stations.

The currents which at or near balance produce the signals are

$$G' = \frac{E''}{4} \cdot \frac{\mu'}{g'' + c''} \text{ in station I,}$$

and

$$G'' = \frac{E'}{4} \cdot \frac{\mu''}{g' + c'} \text{ in station II.*}$$

These expressions follow from the general formulæ by fulfilling the regularity equation (VIII.) for both stations, and, in addition, the balance-conditions.

\* For balance in station II. the current passing through station I. is

$$G' = E'' \frac{b''}{K''} \mu' \psi',$$

$$\frac{K''}{n''} = \psi';$$

$$\therefore G' = E'' \frac{b''}{n'' \psi''} \mu' \psi'.$$

But  $\psi' = \psi''$  on account of  $a = d = g = f$  in each station;

$$\therefore G' = E'' \frac{b''}{n''} \mu'.$$

But  $n'' = 4g''(g' + b'')$ ,

and dividing by  $b''$  we get

$$G' = \frac{E''}{4} \cdot \frac{\mu'}{g'' + \frac{g'^2}{b''}}.$$

But  $g''^2 = b''c''$  on account of balance in station I.;

$$\therefore G' = \frac{E''}{4} \cdot \frac{\mu'}{g'' + c''}.$$



Multiplying now  $G'$  by  $\sqrt{g'}$  and  $G''$  by  $\sqrt{g''}$ , we get

$$P' = \frac{E''}{4} \cdot \frac{\sqrt{g'}}{g'' + c''} \mu',$$

$$P'' = \frac{E'}{4} \cdot \frac{\sqrt{g''}}{g' + c'} \mu'',$$

the magnetic moments of the two instruments in Nos I. and II. stations respectively; and considering that

$$\frac{\mu'}{g'' + c''} = \frac{\mu''}{g' + c'} = \frac{i}{Q},$$

where  $Q = (g' + l')(g'' + l'') + i(g' + g'' + l' + l'')$ , we may write the two above expressions as

$$P' = \frac{E''}{4} \cdot \frac{i}{Q} \sqrt{g'},$$

$$P'' = \frac{E'}{4} \cdot \frac{i}{Q} \sqrt{g''}.$$

The first expression has clearly an absolute maximum with respect to  $g'$ , and the second with respect to  $g''$ ; but these two maxima cannot be simultaneously fulfilled, and do not therefore represent a solution in this particular case. But if we consider that during a *duplex* signal both the instruments  $g'$  and  $g''$  are in circuit, while during a *single* signal, though not both the instruments yet certainly their equivalent in resistances is in circuit, it will be clear why simultaneous maxima of the two single expressions are *not* possible. It represents simply the more general case to which the question belongs of making the magnetic moments of two instruments, connected up in the same single circuit, maxima. In this case it is well known we can do nothing more than make the sum of the magnetic moments a maximum; and here therefore we must do the very same.

Adding, then, we get

$$P = P' + P'' = \frac{i}{4} \frac{E'' \sqrt{g'} + E' \sqrt{g''}}{Q},$$

which expression has a maximum with respect to both  $g'$  and  $g''$  considered as independent variables; and such indeed, according to the nature of the problem, they really are.

Thus, differentiating  $P$  with respect to  $g'$  and  $g''$ , we get

$$\frac{dP'}{dg'} = Q - 2 \sqrt{g'} \left\{ \sqrt{g'} + \frac{E'}{E''} \sqrt{g''} \right\} \frac{dQ}{dg'} = 0,$$

\* This can be easily shown by substituting for  $\mu'$ ,  $\mu''$ ,  $c'$ , and  $c''$  their actual values.

and

$$\frac{dP}{dg''} = Q - 2\sqrt{g''} \left\{ \sqrt{g''} + \frac{E''}{E'} \sqrt{g'} \right\} \frac{dQ}{dg''} = 0.$$

But as the same kind of instruments are employed in both the stations, we require evidently also the same force in both to produce the signals, no matter what the state of the line may be.

Thus we must put\*

$$P' = P'',$$

or

$$\begin{aligned} \frac{E''}{4} \frac{\sqrt{g'}}{Q} &= \frac{E'}{4} \frac{\sqrt{g''}}{Q}, \\ \therefore \frac{E''}{E'} &= \frac{\sqrt{g''}}{\sqrt{g'}}. \end{aligned}$$

Substituting this value for the proportion of the electromotive force, we get

$$Q - 4g' \frac{dQ}{dg'} = 0,$$

and

$$Q - 4g'' \frac{dQ}{dg''} = 0;$$

but

$$\frac{dQ}{dg'} = g'' + l'' + i,$$

and

$$\frac{dQ}{dg''} = g' + l + i.$$

Substituting these values in the above equations and reducing, and further dividing the first equation by  $l' + i$  and the second by  $l'' + i$ , we get at last

$$l'' + \frac{il'}{i + l'} + g'' - 3g'' \left( 1 + \frac{g''}{l'' + i} \right) = 0,$$

and

$$l' + \frac{il''}{i + l''} + g' - 3g' \left( 1 + \frac{g'}{l' + i} \right) = 0.$$

Put

$$l'' + \frac{il'}{i + l'} = L'', \text{ measured conduction from station II.,}$$

\* This supposition in the case of a perfect line is fulfilled by itself, since then the two instruments are not only of the same kind, but absolutely identical.

and

$$l' + \frac{il''}{i+l''} = L', \text{ measured conduction from station I.}$$

Thus the two equations which determine the absolute magnitude of  $g'$  and  $g''$  respectively are

$$L' + g' - 3g' \left( 1 + \frac{g'}{l' + i} \right) = 0,$$

and

$$L'' + g'' - 3g'' \left( 1 + \frac{g''}{l'' + i} \right) = 0;$$

from which  $g'$  and  $g''$  can be expressed—namely,

$$g' = -\frac{1}{3}q' + \frac{1}{3}\sqrt{q'(3L' + q')}, \quad . \quad . \quad . \quad (X')$$

and

$$g'' = -\frac{1}{3}q'' + \frac{1}{3}\sqrt{q''(3L'' + q'')}, \quad . \quad . \quad . \quad (X'')$$

where

$$q' = i + l',$$

and

$$q'' = i + l''.$$

Supposing now  $i = \infty$ , or the insulation perfect, we have  $L' = L'' = L$ , and

$$g' = g'' = g = \frac{L}{2},$$

the former *special* solution.

But so long as  $i$  is not infinite,  $L'$  and  $L''$  may be different from each other, and therefore also  $g'$  different from  $g''$ ; and further,

$$g' = \frac{L'}{2}$$

and

$$g'' = \frac{L''}{2}$$

will be somewhat too large. These values, however, will represent a very close approximation in the case of any line in tolerably good electrical condition; and as a line worked *duplicè* represents two lines, it can always be afforded to select the best sections, when the above values for  $g'$  and  $g''$  will be sufficiently correct for all practical purposes, especially if it be remembered that when once  $g'$  and  $g''$  have been fixed they cannot be easily altered, and that therefore  $L'$  and  $L''$  must be invariably certain averages, either for the whole year or for certain seasons. This, however, belongs more to the practical application than to the theory of duplex telegraphy.

The resistance of the  $b$  branch in each station can now be easily calculated from the balance equations and the values given for  $g'$  and  $g''$ .

The value of the  $b$  branch must be calculated in order to be able to ascertain that *maximum* part of  $b$  which will have to be made variable in increments for the purpose of adjusting balance; and to this interesting question we shall revert further on.

The general solution of the problem might now be considered complete if it were not for the currents which produce the signals, of which we do not know as yet with certainty that we have the maxima in the solution given above. It must, however, be understood that this solution represents the *only true one* from our physical point of view, and that, if it should not be identical with that giving the maxima currents when considered generally by themselves from the beginning, the solution would not be thereby invalidated, but only the duplex method in question would prove to be not quite so perfect as could be desired. The sequel, however, will show that the relation  $a=d=g=f$  represents also the maxima currents that are possible under the circumstances. As this investigation is of great importance in forming a correct opinion of the value of the method, it will be fully gone into.

*Maxima Currents.*—When considering the question of currents for any telegraphic circuit, the two conditions which invariably should be fulfilled are:—

*First.* Greatest possible constancy of current.

*Secondly.* Maximum current.

How far these two conditions can be fulfilled simultaneously depends clearly on the special circuit and the special arrangements adopted; but so much is certain, that, from a practical point of view, the first condition (constancy of current) will always be of far greater importance than the second, inasmuch as the required strength of currents can be obtained by employing cells efficient in kind, sufficient in number, and properly arranged to suit requirements.

Thus in our case, when we consider the currents which produce the signals in duplex telegraphy, before going to the condition of maximum current we must ascertain first the condition of *greatest possible constancy* of current.

Now it has been proved before that *immediate balance* in each station is requisite in order to make the effect of any disturbance on the receiving instrument as small as the circumstances will allow of. But as these disturbances were considered with respect to *one* and the *same* instrument (*i. e.* independently of the magnetic moment), these disturbances are then simply due to the disturbances in the signalling current; from which it follows

at once that the fulfilment of the *immediate balance* condition is required also in order to have the *greatest possible constancy* in the signalling current. Thus, when investigating the question of maxima currents, we are justified in presupposing the rigid fulfilment of the immediate balance for both stations, *i. e.*

$$ad - gf = 0.$$

Further, as it has been shown before that the fulfilment of the regularity-condition

$$a = d = g = f$$

for both stations does make the effect of the disturbances still *smaller*, we have only to investigate the current at balance, and to show that the condition of maximum current becomes identical with the regularity-condition, whence it would follow that the duplex method under consideration is perfect in every conceivable respect.

The question to be solved stands, therefore, as follows:—

*Two signalling currents, the expressions of which are known, have to be made simultaneous maxima, while the different variables are linked together by four condition equations.*

Thus

$$G' = E' \frac{b''}{k''} \mu' \psi',$$

the current which produces single and duplex signals in station I.;

$$G'' = E'' \frac{b'}{k'} \mu'' \psi'',$$

the current which produces single and duplex signals in station II.

$$a'd' - b'c' = 0, \quad . \quad . \quad (1)$$

balance in  $g'$ , station I.;

$$a''d'' - b''c'' = 0, \quad . \quad . \quad (2)$$

balance in  $g''$ , station II.;

$$a'd' - g'f' = 0, \quad . \quad . \quad (3)$$

$$a''d'' - g''f'' = 0, \quad . \quad . \quad (4)$$

immediate balance in both stations.

} Condition equations.

Now  $c'$  is a function of  $\rho''$ ; but, on account of equation (4),  $\rho''$  is independent of  $b''$ ; thus  $c'$  is also independent of  $b''$ . In the same way it follows that  $c''$  is independent of  $b'$ ; thus  $b'$  and  $b''$  can be explicitly expressed at once, and from the four condition equations we have

$$b' = \frac{a'd}{c'},$$

$$b'' = \frac{a''d''}{c''},$$

$$f' = \frac{a'd'}{g'},$$

$$f'' = \frac{a''d''}{g''};$$

and substituting these values in the expressions for  $G'$  and  $G''$ , we get

$$G'^* = E'i \cdot \frac{a'g''}{\{c''(a'' + g'') + a''(g'' + d'')\} \{q'(a' + g') + a'(g' + d')\}},$$

$$G''^* = E'i \cdot \frac{a''g'}{\{c'(a' + g') + a'(g' + d')\} \{q''(a'' + g'') + a''(g'' + d'')\}},$$

where

$$q' = i + l',$$

$$q'' = i + l''.$$

Put

$$\frac{g''}{g'} = k,$$

and substitute in the first expression

$$g'' = kg',$$

in the second

$$g' = \frac{g''}{k},$$

\* If in these two expressions we put

$$i = \infty,$$

and remember that then

$$a' = a'' = a,$$

$$d' = d'' = d,$$

$$g' = g'' = g,$$

and

$$c' = c'' = c = L + \rho,$$

while

$$\rho = \frac{a(g+d)}{a+g},$$

we get

$$G' = G'' = G = E \frac{ag}{\{L(a+g) + 2a(g+d)\} \cdot (a+g)},$$

the expression of the current which produces the signals (single and duplex) through a perfect line, as was given in the first part of this investigation (vol. xlviii. p. 136).

when we get

$$G' = E'ik \cdot \frac{a'g'}{\{c''(a'' + g'k) + a''(d'' + g'k)\} \{q'(a' + g') + a'(g' + d')\}},$$

$$G'' = E'i \cdot \frac{a''g''}{\{c'(g'' + a'k) + a'(g'' + d'k)\} \{q''(a'' + g'') + a''(d'' + g'')\}}.$$

Now it will be seen that  $G'$  has clearly a maximum with respect to  $g'$ , while  $G''$  has a maximum with respect to  $g''$ ; thus, if we take  $g'$  as the only variable in  $G'$  ( $k$  constant) and differentiate with respect to  $g'$ , we get

$$\frac{dG'}{dg'} = 0;$$

and if we take  $g''$  as the only variable in  $G''$  and differentiate, we get

$$\frac{dG''}{dg''} = 0.$$

These two equations must be fulfilled simultaneously in order to have the simultaneous maxima of the two currents in question.

Executing the differentiation, and resubstituting for  $k$  its value  $\frac{g''}{g'}$ , we get, after reduction,

$$\begin{aligned} a'a''(c'' + d'')(q' + d') - g'g''(a' + q')(a'' + c'') \\ - g'(a'' + g'')\{q'(a' + g') + a'(g' + d')\} \frac{dc''}{dg'} = 0, \end{aligned}$$

and

$$\begin{aligned} a'a''(c' + d')(q'' + d'') - g'g''(a'' + q'')(a' + c') \\ - g''(a' + g')\{q''(a'' + g'') + a''(g'' + d'')\} \frac{dc'}{dg''} = 0, \end{aligned}$$

while

$$\begin{aligned} \frac{dc''}{dg'} &= \frac{i^2}{(q' + \rho')^2} \cdot \frac{a'(a' - d')}{(a' + g')^2}, \\ \frac{dc'}{dg''} &= \frac{i^2}{(q'' + \rho'')^2} \cdot \frac{a''(a'' - d'')}{(a'' + g'')^2}. \end{aligned}$$

Now the terms in the two equations which have  $\frac{dc''}{dg'}$  and  $\frac{dc'}{dg''}$  for factors become independently zero—the first for  $a' = d'$ , and the second for  $a'' = d''$ ; and substituting these values for  $d'$  and  $d''$  in the other two terms, both become zero for

$$a'a'' - g'g'' = 0;$$

whence it follows that

$$\begin{aligned}a' - d' &= 0, \\ a'' - d'' &= 0, \\ a'a'' - g'g'' &= 0\end{aligned}$$

is one of the simultaneous solutions of the two equations\*.

Thus, substituting for  $d'$  its value  $a'$ , and for  $d''$  its value  $a''$ , we get

$$\begin{aligned}G' &= E''i \frac{a'g''}{(c'' + a'')(a'' + g'')(a' + g')(a' + q')}, \\ G'' &= E'i \frac{a''g'}{(c' + a')(a' + g')(a'' + g'')(a'' + q'')}.\end{aligned}$$

The first equation has clearly a maximum with respect to  $a'$ , and the second with respect to  $a''$ ; namely,

$$\frac{dG'}{da'} = 0, \text{ which gives } a' = g',$$

and

$$\frac{dG''}{da''} = 0, \text{ which gives } a'' = g''.$$

Thus it follows generally that  $a = d = g$  represents a maximum of the currents; and this, in consequence of the immediate balance, gives at last

$$a = d = g = f,$$

the known regularity-condition, which thus has also to hold good in order to make the two currents  $G'$  and  $G''$  simultaneous maxima.

The *first problem* for the bridge method has therefore now been generally solved; and the results are expressed by the following formulæ:—

$$a = d = f = g = w + \beta,$$

$$g = H \left( \sqrt{1 + \frac{L}{H}} - 1 \right),$$

where

$$H = \frac{q}{3} = \frac{l+i}{3}.$$

When the insulation is perfect ( $i = \infty$ ), the results revert to those originally obtained in the special solution, viz.:—

\* The other solutions, however, which are possible from a mathematical point of view, are impossible with respect to the physical problem; for the quantities, being all electrical resistances, must be taken with the same sign, say positive.



$$a = d = f = g = w + \beta,$$

$$g = \frac{L}{2},$$

$$b = \frac{L}{6}.$$

It will be clear that the given solution fulfils the following conditions, which are necessary and sufficient to place duplex telegraphy on a par with single telegraphy.

- i. *Any variation in the resistance of the line has the least possible disturbing effect on the receiving instrument.*
- ii. *Any disturbance can be eliminated by a single adjustment in the  $b$  branch without disturbing balance in the distant station.*
- iii. *Maximum magnetic moment of the receiving instrument.*
- iv. *Maximum current.*

There seems to me to be no other method that can fulfil all these conditions simultaneously; and the “double-balance”\* method must therefore be pronounced perfect in every conceivable respect. I am convinced that if the general problem of duplex working were investigated by means of the variation calculus, the *double-balance* method would come out as the *final* and *only* solution†.

#### *Addendum—Historical.*

When reading this paper before the Asiatic Society (on the 4th

\* I have called this method the “double-balance” method, since there are two balances to be fulfilled in each station—namely, balance in the  $b$  branch for the arriving current, and balance in the  $g$  branch for the outgoing current.

† The double-balance method was introduced on one of the important Bombay-Calcutta main lines in June last. Since then this duplex method has been working so satisfactorily and with such regularity and speed, even during the worst time of the year (south-west monsoon), when necessarily the insulation as well as the inductive capacity of lines are so enormously variable, that about its thorough practicability no doubt can be entertained; and Colonel Robinson, Director-General of Telegraphs in India, has consequently decided to introduce this duplex method also on the other long main lines of India.

At present the apparatus for the Bombay-Madras line (worked direct 800 miles) is almost finished, and the apparatus for Calcutta-Rangoon is under manufacture.

The Calcutta-Bombay main line is worked duplicè with Jabalpur only in translation; distance between Calcutta and Jabalpur 850 miles; distance between Jabalpur and Bombay 640 miles. The wire is almost throughout No.  $5\frac{1}{2}$  B. W. G. (diam. =  $5\frac{1}{4}$  millims.).

This experiment, on such a large scale and made under the most unfavourable meteorological conditions, has proved to evidence the practicability of the *double-balance* method, which certainly will invariably succeed on any line where single telegraphy is possible.

of February, 1874), and further, when editing the First Part for publication in the Journal of the Society, I was unacquainted with the fact that a most complete history of duplex telegraphy had been published by Dr. Karl Eduard Zetzsche\* (Leipzig, 1865). According to Professor Zetzsche†, the bridge method of duplex telegraphy was already invented in 1863 by Maron, a Prussian telegraph-inspector; and Dr. Zetzsche very truly remarks that the bridge method would seem to be that least affected by variations in the resistance of the line. To this, from an historical point of view, most valuable book I refer the reader. It is to be hoped that an English translation of it may soon be published.

[To be continued.]

# XVI. The Eruption of Etna on the 29th of August, 1874.

By Professor ORAZIO SILVESTRI, of Catania‡.

IN a short account published by me on the 1st of July, 1874 (see No. 56 of the *Gazzetta del Circolo dei Cittadini*, Catania, July 12, 1874; also *Bullettino del Vulcanismo Italiano*, fascicolo 6, 7, Rome, July and August 1874; also *Bollettino del R. Comitato Geologico d'Italia*), of the eruptive phenomena which have been observed since last May in the interior of the great central crater of Etna, I expressed an opinion which attracted such general attention as to be quoted in the principal Italian and foreign journals, to the effect that an early outbreak on the Mongibello side, and a great eruption immediately after, were to be expected. This opinion has been fulfilled in less than two months, but fortunately (as I am about to relate) under such conditions as not to produce serious damage, except the consequences of the fear and terror which are generally excited by the more formidable phenomena of this mighty volcano.

After an uninterrupted succession of eruptive phenomena in the central crater, which has in consequence undergone remarkable modifications, at 4 o'clock on the morning of Saturday, August 29, the rural population scattered round the base or on the slope of the mountain on its northern side, even beyond the villages as far as the cultivated belt reaches, in a semicircle of about 80 kilometres, were awakened by subterranean noises, which were speedily followed by two shocks of earthquake, threatening

\* *Die Copiertelegraphen, die Typendrucktelegraphen, und die Doppel-Telegraphie, ein Beitrag zur Geschichte der electrischen Telegraphie*, von Dr. Karl Eduard Zetzsche: Leipzig, 1865.

† Page 125 in the work quoted.

‡ Translated from a pamphlet published by Lorenzo Rizzo, Largo Spirito Santo, Catania (1874). Communicated by Professor H. E. Roscoe, F.R.S.

the destruction of their houses. Those who, alarmed, beat a hasty retreat into the open country, might observe near the crest of the mountain a column of thick black smoke and burning matter which was driven into the air with great impetus and fell again, scattered by the wind, the lighter portions in the form of small scorïæ and sand at a considerable distance. Shortly afterwards this column appeared, to those looking from north to south, as if it became larger at the base, whilst looking from east to west there seemed to be numerous columns inclined slightly towards the north. These, like the first, consisted of thick smoke and burning matter, which in the darkness of night looked like a grand display of fireworks with a constant emission of colossal rays.

This phenomenon was at the same time accompanied by those rumblings which usually manifest themselves when the lava is about to burst forth from the earth, and lasted with great intensity for seven hours on the 29th, from 4 till 11 A.M. For the rest of that day, and during the night of the 29th, the violence of the outbreak diminished; and on Sunday the 30th its force was much weakened; and the following night there was no longer any noise heard, and where the columns of fire had been nothing was seen but smoke, whilst smoke only was emitted by the great central crater.

The first signs of a great eruptive paroxysm had spread consternation in people's minds, as it seemed there could be no longer any doubt that a great eruption of Etna was about to take place, and that it would last for a long time, as is usually the case when the outbreak occurs on the side of the mountain. Moreover a great and lasting lateral eruption, when it occurs at a great elevation, almost invariably produces serious damage, burning up woods and fields, and destroying all on the surface over which the lava flows.

However, as I have said, the eruption, after lasting seven hours, began unexpectedly to abate; and so rapidly did this proceed, that in the short space of two days nothing was left of it but some secondary phenomena.

To minds already alarmed there remained, however, a cause of terror even when the flames had ceased, and one which kept them in some uneasiness for a fortnight, namely the frequent earthquakes, which commenced at 11 or 11½ on Sunday, August 30, at the same time that the eruption began to abate, and agitated the ground of this neighbourhood, and continued to do so incessantly for the first eight days. Those who at this time visited the country lying north of Etna received a most dismal impression. All the inhabitants, poor and rich alike, have forsaken their dwellings; the streets and squares and the

neighbouring fields are encumbered with beds and tents, and with huts formed in a thousand ways, in which whole families have taken refuge, and temporary altars as a substitute for the churches now closed to the worshippers. This forced emigration of the inhabitants from their houses is perhaps no longer necessary, as the shocks of earthquake have become less felt and less numerous; and in fact even during the first few days, when they were the strongest, the shocks, being simply undulatory and not upheaving, did little damage beyond some cracks in a few old walls. But experience, by which the people are ruled, has habituated the country folks to dread their burning mountain, which, however, being with its fruitful soil the cause of their wealth, they will not abandon. They rather resign themselves with a sort of indifference to the tribute of sacrifice which Etna sometimes requires of them.

After this preface I will now give an abstract of the observations I made on the scene of the eruption, which contains the exact details of the volcanic disturbance we have witnessed at Mongibello.

On the day in question (August 29), at 4 P.M., when the two powerful shocks of earthquake were felt, starting from the elevated base of the great central crater, at a point on the north side where the crest which surrounds and limits the hollow (known as the elliptical crater) presents a remarkable depression, and descending for a distance of five kilometres to the level of the so-called "Timpa Rossa" and of the Monte Nero, the earth was rent by the violent shock, which, to judge from its effects, must have been of extraordinary force; this produced a long chasm, the axis of which was  $8^{\circ}$  north of east. The centre of impulsion was on the northern flank of the mountain, 2450 metres above the level of the sea, and exactly between the two hills of lava called the Fratelli Pii (or otherwise I Due Pizzi) and an old crater known by the name of the Monte Grigio. At this point, where the dynamic effect on the earth was the greatest, the chasm was from 51 to 60 metres in breadth; and going further down this was gradually reduced to 30, 20, 15, 10, 5, and 3 metres, till it ended, having altogether a length of about 3 kilometres. From this point upwards, toward the elevated base of the central crater, where the earth had presented greater resistance, the continuation of the upheaval was shown by jets of smoky vapour which appeared in the same direction. That at this height of 2450 metres the greatest volcanic force has been expended is shown by the formation of a new mound, or crater, the upper edge of which has an elliptical form, and which has its major axis in the direction  $8^{\circ}$  north-east of the chasm. The upper edge of this new crater has a circumference of about

300 metres and a diameter of about 100 metres, and a height of 50 metres from its base: this, with an inclination of the sides of about  $30^\circ$ , gives us a base of 860 metres circumference; and the mound occupies therefore an area of 117,734 square metres. This crater, which looks like a new mountain, is formed of a heap of fragments of doleritic and prehistoric labradoritic lavas of a grey colour, which have been brought up from a great depth by the force of the outbreak of modern lava, which seems in parts to have kneaded the other together. It is singular to see all round this new crater for an area of half a kilometre radius, blocks, lumps, and larger or smaller fragments of this prehistoric lava of a clear grey colour scattered about, contrasting with the present lava, which is very black, and with which they seem here and there to be lined; so that we thus have the lavas of two widely distant epochs brought into contact—one representing an eruption which no man can have witnessed, the other produced by an eruption of today.

The interior of the crater exhibits the usual funnel-shaped form; but its depth has no visible limits. We look across a dark cavernous mouth on whose walls may be seen (as far as the light reaches) jutting out strata of lava of various epochs one above another. The structure and origin of this crater are of great scientific interest.

Moving from this culminating point and following the chasm on which it is placed, we find that for some distance it passes across a stream of lava of uncertain date, but of the past century, for a distance of about half a kilometre.

Here near the base of the crater the chasm presents a maximum breadth of from 50 to 60 metres; and here we see ten small craters of some considerable depth, which, placed one after the other, resemble a row of button-holes. Of these, those nearest to the crater are wide abysses 25 or 30 metres in diameter; the others have a mean diameter of about 10 metres.

After these ten openings, constituting the first group of small craters, and as we continue to follow the chasm as it grows narrower, we find, after a short interval produced by an inequality of the ground, four others near each other, their mean distance from each other being from 2 to 3 metres. Then at a distance of 10 metres further on we find four others in the same proximity to each other as the first four; and these eight together form a distinct group.

Another interval of about 50 metres then occurs, the chasm continuing without any further openings until again four other small craters appear very near each other, three being on the principal chasm. The chasm at this point crosses the side of one of the hills called the Fratelli Pii or the Due Pizzi, which con-

sist of solid lava, and the hill has in consequence been split up in various directions; and here again one of the eruptive openings occurs slightly lateral to the principal chasm. These four last small craters form a third group. The diameter of the opening of the second and third groups varies from 1 to 3 metres.

Following the chasm thus far from the crater (that is, for the length of half a kilometre), we find in this way twenty-two eruptive openings, placed along a line in three groups, existing on a nearly flat surface, the mean elevation of which above the sea is 2440 metres, which is now covered with fragments of old lava and with cinders and scoria from the new lava.

Proceeding from this flat ground, which seems a sort of tableland, towards the north, we meet with a declivity at an angle of 13 to 14 degrees, formed by the great current of solid lava of the year 1614. This is full of numerous and recent cracks, and in some parts is completely broken up by the various earthquakes which have taken place. Still we can trace the continuation of the principal chasm through it, and in this continuation for a distance of about 600 metres there are no openings caused by a more active volcanic force; but at an elevation of 2170 metres we find a fourth group of five small craters from 2 to 3 metres in diameter and of an unknown depth, from which a torrent of lava has escaped which has flowed down to a distance of 150 metres with an average width of 60 metres, and having a thickness of 2 metres. This lava-stream, following the inclination of the ground, has flowed towards a branch of the lava of 1809, which, standing out prominently, has checked it; and it has then spread itself out at the base but without passing beyond it. The chasm, however, crosses it, and continues thence downwards through the aforesaid great current of 1614 for another half kilometre; in this distance appears a fifth group of three small craters at 2150 metres elevation. This is the most active group of all, as it has sent forth a lava-stream about 400 metres in length, 80 in average width, and 2 in thickness; and this forms two short branches deviating towards the west.

Finally, the last portion of the chasm in a length of about 50 metres presents a sixth and last group of five craters very near together, from 1 to 4 metres in diameter, which have emitted a large quantity of cinder and some fragments of scoria. This sixth group of craters marks the lower limit of the chasm visible on the surface of the soil, this point being at 2030 metres above the level of the sea, 12 kilometres distant.

To sum up what has been said, we have:—

1st. The most remarkable rent in the ground, extending from the lower edge of the new crater in the form of a principal chasm slightly tortuous in direction, the most important part of which

extends for a length of 3 kilometres, with a width varying from 60 to 3 metres. This is set in the direction N. 8° E., and if extended upwards would join on to the central crater of Etna like a sort of ray, which, prolonged downwards to the extreme circumference of the mountain, would meet the old crater of Majo. Besides this principal chasm there are innumerable cracks which seem collateral and radiating from the centres of strong dynamic action.

2nd. Next to this chasm the principal effect of the eruption is the new mountain, raised up in a few hours, which constitutes the crater, formed of a regularly shaped heap of blocks and fragments of old labradoritic lavas brought up by the shock from the great depths and partly cemented together by the new lava. Then also there are the six groups of small craters, numbering in all thirty-five, which, following the eruption, constitute a system of elevated crater-shaped mounds.

3rd. The lava, which, besides that forming the crater, and that which is spread over a vast belt in the form of cinders, scoria, and sand, also constitutes two torrents, one 150 metres long, the other 400 metres.

According to the above measurements of these torrents and of the crater, we find that the following quantity of lava was produced by the eruption:—

By the first torrent, in cubic metres . . .	18,000
By the second torrent, „ . . .	64,000
By the crater „ „ . . .	1,269,000
Total mass brought to the surface, in cub. met.	1,351,000

All this mass occupied a surface of:—

For the first torrent of lava, in square metres .	32,000
Second torrent, „ „ „ „ .	90,000
Crater „ „ „ „ .	117,734
Total, in square metres . . . . .	239,734

That is, equal in extent to 24 hectares, yet without doing any damage, the soil here being entirely formed of bare rocks.

If, however, the lava had been able to continue its course, it would soon have come into contact with a wood lying between Randazzo and Lingua Glossa.

4th. The old lavas, irrupted from strata deep in the earth, consist of a pale-coloured dolerite, and grey and compact augitic labradorite, identical with that which forms part of the backbone of Etna and crops up in the exposed strata or in the banks of the Valle del Bove. The new lava, on the contrary, is more or less full of scoria, of an augitic character and of a black colour, like all modern lavas; and it often has a metallic lustre. It is also mag-

netic, and has a specific gravity of 2·3636 at 25° C. The lava-bed, although its course was a very short one, nevertheless had a surface-temperature of 70°, whilst at the depth of half a metre it had a temperature of 90°; and the temperature increases at the points where the secondary phenomena are found. The outward manifestations of the eruption at the date of which I write may be said to be over, since the mouth of the new crater and the thirty-five eruptive openings of the chasm, though they are still open, only emit a small quantity of vapour, now in an increasing, now in a decreasing quantity, similar to that observed in the great central crater. The activity observed in the central crater from the end of May to the latter days of August, when the eruption broke out, has now quite ceased. This sudden paroxysm of Etna, which in such a short time (in less than a day) has left the mark of a formidable eruption, has furnished us with a curious fact in the special history of our volcano. It was known that from the chief crater, in consequence of its elevation of 3314 metres above the sea, there could only be eruptions of short duration; but it was also known that if the volcanic force reached such a degree of intensity as to produce a lateral outbreak, the eruptions that followed would probably be of long duration, as they had been formerly in this and in preceding centuries, similar to those which usually happen in Etna at intervals of ten or twelve years. How can we then explain the cessation of the recent phenomenon?

If upon such a subject an opinion may be given which likewise goes to explain the occurrence of earthquakes permanently which agitated the ground after the eruptive activity had ceased, I would suggest that the violent shock felt on the N.N.E. side of the mountain may have created an outlet extensive and deep enough for the lava breaking forth from the axis of eruption at Mongibello to find a more easy channel into subterranean caves and channels than to be forced more slowly out to the surface.

This idea would be confirmed by seeing all the preparation for an eruption with the thirty-five mouths remaining inactive, though open and smoking, and by hearing in their immediate neighbourhood a deep noise as of a flowing subterranean mass. It would also tend to support the theory which maintains that the cause of earthquakes is the completion of some subterranean eruption\*, if we may so designate a movement of fluid and gaseous matter in the interior of the earth.

Such a conjecture would perfectly agree with the phenomenon of the shocks which occurred when the outward flow of the eruption continued nearly in full force; for it is generally the case

\* This theory is also maintained by Sig. Rudolph Falb, of Vienna, who after my prophecy of July came to stay near Etna to observe the new eruption.



in eruptions elsewhere that the outward flow of the lava ceases when the shocks are felt.

It suffices to mention the earthquakes which agitated the eastern side of Etna when the external manifestations of the eruption of 1865 had just ceased, specially that terrible one in the neighbourhood of Giarre, which destroyed the village called Fondo Macchia. These earthquakes gradually decreased in number and intensity in the direct ratio which is observed in the movement of the lava in an eruption, which by gradually checking itself soon ceases altogether. The eruptive apparatus, still hot and smoking and placed thus along an abyss of lava, we must believe will now remain inactive, and that a great eruption is not to be expected as imminent; since it seems strange to admit that when the intensity of the volcanic force has reached the point of creating this imposing apparatus, it should then have chosen to interrupt its course after a few hours' eruption, in order to resume it again afterwards. The truth is more probably, as I have said, that in the dislocation and breaking up of the consolidated strata of the mountain the mass of lava has found a way of penetrating more quietly into the caverns of the earth, deviating from the axis of eruption, and deriving its mechanical force from the gases and vapours, from which in time it may acquire such dynamic energy as to cause explosions capable of driving it out to the surface with the ordinary phenomena of eruption.

It is very probable that a future eruption of Etna, when it takes place, will happen on the side of the mountain already opened, where certainly the lava will find less difficulty in coming to the surface.

This last eruption of Etna has enriched the history of volcanoes with a new and important page, and the appearance of this preparation for a great eruption which remains inactive is of interest in the annals of volcanic science. It remains quite unchanged by any emission of volcanic matter, but, remaining fully open, seems to give material testimony to the fact of nature having been surprised and disturbed in one of her great operations. Indeed any one who may wish to form a clear idea of how an explosion in a great volcano, outside of the central crater, begins, and by means of what mechanism it is completed, can now visit and observe with attention the interesting localities of the eruption of August 1874.

This disturbance of Etna which we have described is not an isolated one in the Italian volcanic system.

In the nearest island of Vulcano, after a century's inactivity, a new abyss opened in the large crater nine months before the eruption of Etna (from the 20th of September to the 20th of October, 1873). This was accompanied by an eruption of

cinders and burning matter, together with flames, rumbling, and earthquakes. These phenomena, which had a gradually decreasing course, lasted through all the month of July 1874; and traces of them still remain.

Stromboli also in June last had an unusual eruption, being violently agitated, and throwing out stones as far as the inhabited district which lies underneath it, showing much greater activity than in the little explosions every two or three minutes which characterize its usual action. It seems that Vesuvius also has not remained indifferent to all this; and I saw myself from its crater, as well as from that of Stromboli, a remarkable and unusual amount of thick smoke coming out at the same time that the eruption of Etna took place.

XVII. *On Primary Forms.* By SIR JAMES COCKLE, F.R.S.,  
Corresponding Member of the Literary and Philosophical Society  
of Manchester, President of the Queensland Philosophical Society, &c.\*

1. **C**OMPARING p. 428 of Boole's 'Differential Equations' (1865), and pp. 184 and 190 of the Supplement, with a citation in Mr. Harley's recent paper "On the Theory of Differential Resolvents" (which purports to be reprinted from the Report of the British Association for 1873), it seems to me that Boole did not always use the term *primary* in the same sense. By *primary* I mean integrable, but not through Boole's reductions. By a *factorial substitution* I mean a change of  $y$  into  $Xy$ , where  $X$  is a function of  $x$ . By taking the *criticoid* of a biordinal I mean reducing its middle term to zero and dividing the equation so transformed by the coefficient of its first term. This *criticoidal*† transformation is effected by factorial substitution, not by change of the independent variable. By the equation of the *cæsura*, or briefly the *cæsura*, I mean an equation derived from a given equation by expunging its last term and diminishing by unity the indices of the differential coefficients.

2. The regular forms, as we may term those solved through Boole's reductions, are of two descriptions. In one factors are preserved which in the other are lost. The first description of binomial biordinal may be written

$$\{(\Delta - 2m)(\Delta - 1) - (\nabla + 2n)(\nabla - 1)x^2\}y = 0, \quad (1)$$

where

$$\Delta = D + \beta \text{ and } \nabla = D + \alpha.$$

\* Communicated by the Rev. Robert Harley, F.R.S.

† As to this use of the term *criticoidal*, see my paper "On Hyperdistributives" (Phil. Mag. for April 1872) and the papers connected therewith.

Let

$$\Delta(\Delta-r) \dots (\Delta-nr) = [\Delta]_r^{n+1}.$$

Then

$$[\Delta]_r^{n+1} = (\Delta-nr)[\Delta]_r^n = \Delta[\Delta-r]_r^n;$$

so that if in (1) we replace  $y$  by its equivalent

$$\frac{[\Delta]_2^m [\nabla + 2n]_2^n}{[\Delta]_2^m [\nabla + 2n]_2^n} y,$$

then (1) will take the form

$$[\Delta - 2]_2^m [\Delta + 2n]_2^n \{ \Delta(\Delta - 1) - \nabla(\nabla - 1)x^2 \} Y = 0,$$

where

$$Y = \frac{1}{[\Delta]_2^m [\nabla + 2n]_2^n} y.$$

Hence the solution of (1) is reduced to that of

$$(\Delta - 1 \pm \nabla x)(\Delta \mp \nabla x) Y = 0. \quad \dots \quad (2)$$

But a particular integral of (2) is

$$Y = x^{-\beta} (x+1)^{\beta-\alpha-1}.$$

Consequently (1) has a particular integral of the form

$$(x+1)^\lambda R(x) = y,$$

where  $R(x)$  is rational.

3. This form is included in  $e^{\int \phi(x) dx}$ , where  $\phi(x)$  is rational. So, too, is that of the solution of the first case of the second description of regular forms, viz.

$$\{ (\Delta - 2n)(D + \beta) + \Delta(D + \alpha)x^2 \} y = 0, \quad \dots \quad (3)$$

where  $\Delta = D +$  any constant. For if we replace  $y$  by  $\frac{[\Delta]_2^n}{[\Delta]_2^n} y$ ,

then (3) reduces to

$$[\Delta]_2^{n+1} G \frac{1}{[\Delta]_2^n} y = 0, \quad \dots \quad (4)$$

where

$$G = D + \beta + (D + \alpha)x^2.$$

Hence a particular integral of (3) will be given by

$$y = [\Delta]_2^n G^{-1} 0.$$

But

$$G^{-1} 0 = x^{-\beta} (x^2 + 1)^{\frac{\beta - \alpha - 2}{2}}.$$

Consequently (3) will have a particular integral of the form

$$y = (x^2 + 1)^\lambda R(x),$$

where  $R(x)$  is rational, and therefore of the form  $e^{\int \phi(x) dx}$ , where  $\phi(x)$  is rational.

4. The second case of the second description, viz.

$$\{\Delta(D+\beta) + (\Delta-2n)(D+\alpha)x^2\} \frac{[\Delta]_2^n}{[\Delta-2]_2^n} y = 0, \quad . \quad . \quad (5)$$

reduces to

$$\frac{G[\Delta]_2^n}{[\Delta-2]_2^{n-1}} y = 0,$$

or

$$G[\Delta]_2^n y = 0; \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which last is solved, with redundant constants (conf. *op. cit.* p. 421, et Suppl. p. 189), by

$$y = x^m (C_0 + C_2 x^2 + \dots + C_{2n-2} x^{2n-2}), \quad . \quad . \quad (7)$$

if we make  $\Delta = D - m$ . And the redundancy is got rid of if in (5) we substitute for  $y$  the dexter of (7). For  $\Delta$  and  $\Delta - 2n$  respectively annul the terms  $C_0 x^m$  and  $C_{2n-2} x^{m+2n}$ , leaving all the  $n$  quantities  $C_0, C_2, \dots, C_{2n-2}$  to satisfy the remaining  $n-1$  homogeneous conditions. Thus (5) has a particular integral, which is of the form  $R(x)$ , and therefore of the form  $e^{\int \phi(x) dx}$ ;  $R(x)$  being rational and entire, and  $\phi(x)$  rational.

5. The first primary form of Boole (*op. cit.* p. 428) may, without loss of real generality, be written

$$(1+x^2) \frac{d^2 y}{dx^2} + x \frac{dy}{dx} - n^2 y = 0, \quad . \quad . \quad . \quad (8)$$

$$\{D(D-1) + [(D-2)^2 - n^2] x^2\} y = 0. \quad . \quad . \quad (9)$$

But this form is not truly primary when  $n$  is an integer or the half of an integer, the latter case corresponding to a quadratic resolvent. And this accords with what precedes. The complete integral of (8) or (9) is

$$C_{+1} (x + \sqrt{x^2 + 1})^n + C_{-1} (x - \sqrt{x^2 + 1})^n = y.$$

Take  $n$  a positive integer and  $C_{+1} = C_{-1}$ . Then  $y$  is rational and entire. Take  $n$  the half of a positive integer. Then

$$\frac{\sqrt{x^2 + 1}}{n} \frac{dy}{dx} = C_{+1} (x + \sqrt{x^2 + 1})^{n-1} - C_{-1} (x - \sqrt{x^2 + 1})^{n-1};$$

and if  $C_{+1} = 1$  and  $C_{-1} = -1$ , then  $\frac{\sqrt{x^2 + 1}}{n} \frac{1}{y} \frac{dy}{dx}$  will become

$$\frac{(x + \sqrt{x^2 + 1})^{2n} + (x - \sqrt{x^2 + 1})^{2n} + 2(-1)^n}{(x + \sqrt{x^2 + 1})^{2n} - (x - \sqrt{x^2 + 1})^{2n}}.$$

In either case\*  $\frac{1}{y} \frac{dy}{dx}$  is rational, and  $\frac{dy}{dx}$  in the former rational and entire. In both cases, therefore,  $y$  is of the form  $e^{\int \phi(x) dx}$ , where  $\phi(x)$  is rational. The proof may be extended to the cases of  $n$ , a negative integer, or the half thereof. In no other cases has (8) or (9) a particular integral of the form  $e^{\int \phi(x) dx}$ . And since (8) and (9), if soluble through Boole's reduction, must fall under one of the three forms (1), (3), or (5), the first primary form is not in general so soluble. The same may be proved for his second primary form.

6. Let

$$\frac{d^2y}{dx^2} + 2a \frac{dy}{dx} + zy = 0, \quad . \quad . \quad . \quad (10)$$

where  $z$  is any function of  $x$ . Suppose that  $2a = -\frac{p}{2z} + C\sqrt{z}$ ,

where  $p = \frac{dz}{dx}$ . Then (10) is reducible to an equation with constant coefficients by a change of the independent variable. The primary (8) is thus soluble. But it may be otherwise solved. Let  $\int_x U$  mean  $\int U dx$ , and let  $P(\int_x \xi \int_x \eta)$  mean the double operation  $\int_x \xi \int_x \eta \int_x \xi \int_x \eta \dots$  continued in *infinitum*. Also let  $y = \psi(x)$  be a particular integral of (10). Then if  $\xi$  be determined from the equation† of the *cæsura*, viz.  $\frac{d\xi}{dx} + 2a\xi = 0$ , and  $\eta$  from

\* The same is true of every case. For (1), (3), and (5), together with the three forms

$$\{(\Delta - 2m)(\Delta - 1) - a^2 x^2\}y = 0, \quad . \quad . \quad . \quad (a)$$

$$\{(\Delta - 2n)(D + \beta) + \Delta x^2\}y = 0, \quad . \quad . \quad . \quad (b)$$

$$\{\Delta(D + \beta) + (\Delta - 2n)x^2\}y = 0, \quad . \quad . \quad . \quad (c)$$

and the six other forms deduced from these by the change of  $x$  into  $\frac{1}{x}$  constitute the twelve forms which the reductions of Boole solve. Both here and in the text  $m$  and  $n$  are integers. The arguments for (a), (b), and (c) respectively are analogous to those for (1), (3), and (5), and show that there is at least one particular integral of the form  $e^{\int \phi(x) dx}$ .

† This method of synthetical solution may give a finite result, a series summable or otherwise, or a suggestion of the form of  $\psi(x)$ , in which a constant or constants are to be determined by substitution. For the terordinal

$$\frac{d^3y}{dx^3} + 3a \frac{d^2y}{dx^2} + 3b \frac{dy}{dx} + cy = 0, \quad . \quad . \quad . \quad (d)$$

where  $a$ ,  $b$ , and  $c$  may be variable, we assume  $y = P \int_x \xi \int_x \eta \int_x \zeta \cdot \psi(x)$ , where  $\psi(x)$  is a particular integral, say zero, and  $\xi$  is determined by the *cæsura*

$\xi\eta + z = 0$ , a complete integral of (10) will be given by

$$y = P\left(\int_x \xi \int_x \eta\right) \psi(x),$$

the arbitrary constant  $C_\xi$  being added after the  $\xi$  integration, and  $C_\eta$  after the  $\eta$  integration. Applying this to the primary

(8), we find  $\xi = \frac{C}{\sqrt{x^2+1}}$  and  $\eta = \frac{n^2}{C\sqrt{x^2+1}}$ . Hence  $C=n$  gives

$\eta = \xi$ ; and if we take the particular integral  $\psi(x) = 0$ , we find

$y = P\left(\int \frac{ndx}{\sqrt{x^2+1}}\right) 0$ . For simplicity add unity after each in-

tegration. Then, whether we evaluate by series, or by treating

$y$  as an integral of the linear equation  $\frac{dy}{dx} - \frac{n}{\sqrt{x^2+1}}y = 0$ , we

have  $y = C_{+1}(x + \sqrt{x^2+1})^n$ ; and in like manner the second corresponding particular integral may be found.

7. Boole seems to have considered the regular and the primary forms as of distinct species. This I attribute in part to his not recognizing, in the theory of the former, any change of the independent variable other than that from  $x$  to  $kx^n$ . Under appropriate changes there is a certain reciprocity which appears to indicate that all the forms are but varieties of one species.

8. All binomial (*op. cit.* p. 430) biordinals may be included in

$$\frac{d^2y}{dx^2} + \frac{2}{x} \frac{a+ex^n}{h+kx^n} \frac{dy}{dx} + \frac{1}{x^2} \frac{f+gx^n}{h+kx^n} y = 0.$$

Taking the criticoid, we have

$$\frac{d^2y}{dx^2} + \frac{L + Mx^n + Nx^{2n}}{x^2(h+kx^n)^2} y = 0;$$

for in this paper I make no explicit change of variable, the form alone of the results being material. The last equation is a trinomial, wherein

$$L = hf + ha - a^2,$$

$$N = kg + ke - e^2,$$

$$M = hg + kf - (n-1)he + (n+1)ka - 2ae,$$

$$\frac{d^2\xi}{dx^2} + 3a \frac{d\xi}{dx} + 3b\xi = 0, \quad \dots \dots \dots (e)$$

and  $\eta$  by the relation

$$\frac{d}{dx} \{\log(\xi^2\eta)\} = -3a, \quad \dots \dots \dots (f)$$

and  $\zeta$  by

$$\xi\eta\zeta = -c. \quad \dots \dots \dots (g)$$

When  $\xi = \eta = \zeta$ , the terordinal is soluble as a primordinal. When (e) is insoluble, a transformation of (d) may possibly have a *cæsura* which is soluble.

expressions which give  $M-L-N$  the value

$$(k-h)(f-g+a-e)+n(ka-he)+(a-e)^2.$$

9. If  $h$  and  $k$  are finite, then by changing  $x$  into  $\left(\frac{h}{k}\right)^{\frac{1}{n}}x$ , dividing, changing  $x$  into  $x^{\frac{2}{n}}$ , and making appropriate changes in the constants, we may without loss of real generality replace the binomial by

$$(1+x^2)x^2\frac{d^2y}{dx^2}+2(a+ex^2)x\frac{dy}{dx}+(f+gx^2)y=0, \quad (11)$$

the trinomial by

$$(1+x^2)^2x^2\frac{d^2y}{dx^2}+(L+Mx^2+Nx^4)y=0, \quad (12)$$

and the accompanying system by

$$L=f+a-a^2, \quad (13)$$

$$N=g+e-e^2, \quad (14)$$

$$M=f+g+3a-e-2ae, \quad (15)$$

$$M-L-N+1=(a-e+1)^2=\mathcal{A}E^2. \quad (16)$$

10. Boole's process reduces (11) to

$$\{D(D-1)+2aD+f\}y + \{(D-2)(D-3)+2e(D-2)+g\}x^2y=0, \quad (17)$$

and if we put

$$A(F-1)=-L, \quad E(E+1)=-N,$$

then (11) is solved through Boole's reductions :

First, if  $A$  and  $E$  are both integers ;

Secondly, if  $\mathcal{A}E-A-E$  is an odd integer.

And (11) is primary :

First, if  $A$  is an integer and  $2\mathcal{A}E$  an odd integer ;

Secondly, if  $E$  is an integer and  $2\mathcal{A}E$  an odd integer.

11. In (12) change the independent variable from  $x$  to  $\tan x$  and take the criticoid of the result. Then (12) is replaced by

$$\frac{d^2y}{dx^2}+(L \cot^2 x + M + 1 + N \tan^2 x)y=0. \quad (18)$$

Now, if by a factorial substitution we pass from a form in which the last coefficient is variable to one in which such coefficient is constant, the two forms may be called conjugate. A conjugate of (18) is

$$\frac{d^2y}{dx^2}+2(A \cot x + E \tan x) \frac{dy}{dx} + Qy=0, \quad (19)$$

where

$$Q = M + 1 - A + E + 2AE = \mathcal{A}^2 - (A - E)^2.$$

Next differentiate (19), replace  $\frac{dy}{dx}$  by  $y$ , and take the criticoid of the result. We have

$$\frac{d^2y}{dx^2} + \{M + 1 - (A + 1)A \cot^2 x - (E - 1)E \tan^2 x - 2A + 2E\}y = 0, \quad (20)$$

of which a conjugate is

$$\frac{d^2y}{dx^2} + 2\{(A + 1) \cot x + (E - 1) \tan x\} \frac{dy}{dx} + Q_1 y = 0, \quad (21)$$

where

$$\begin{aligned} Q_1 &= M + 1 - 2A + 2E - (A + 1) + (E - 1) + 2(A + 1)(E - 1) \\ &= Q - 4A + 4E - 4. \end{aligned}$$

Hence

$$Q_1 = \mathcal{A}^2 - (A - E + 2)^2; \quad (22)$$

and, if neither  $A$  nor  $E$  is an integer, we shall, after performing this process  $n$  times, transform (19) into

$$\frac{d^2y}{dx^2} + 2P_n \frac{dy}{dx} + Q_n y = 0, \quad (23)$$

where

$$P_n = (A + n) \cot x + (E - n) \tan x,$$

and

$$Q_n = \mathcal{A}^2 - (A - E + 2n)^2.$$

But  $Q_n$  will vanish if  $\mathcal{A} \pm (A - E)$  is an even integer. Now the two values of  $A$  are connected by  $A_1 + A_2 = 1$ ; so that if, for instance,  $\mathcal{A} + A_1 - E$  be even, then  $\mathcal{A} - A_1 - E$  will be odd; and the condition coincides with one obtained from Boole's process.

12. For clearness I have supposed that neither  $A$  nor  $E$  is entire. But if both or either be so the process is not stopped. The identities  $c^2 + c = (c + 1)^2 - (c + 1)$  and  $c^2 - c = (c - 1)^2 + c - 1$  give us a choice of conjugates. Let  $E = n$ , then  $\tan x$  disappears from (20) and its conjugate; but, since  $c = -1$  satisfies  $c^2 + c = 0$ , it may be made to reappear. When  $A$  and  $E$  are both entire,  $P_n$  may be made to vanish; and  $Q_n$  is always a constant. I believe that the results of this process are coextensive with the regular results of that of Boole, and that it applies to such forms as

$$\frac{d^2y}{dx^2} + (\tan x + 2C \cot x) \frac{dy}{dx} + K \cot^2 x \cdot y,$$



which, though of the soluble form of art. 6, is regular. It does not apply to

$$\frac{d^2y}{dx^2} + \frac{\cot x}{3} \frac{dy}{dx} + \frac{2}{9}y = 0,$$

which is a coresolvent.

13. But the reciprocity of forms will appear if in (12) we change  $x$  into  $x\sqrt{-1}$ , thus obtaining

$$(1-x^2)^2x^2 \frac{d^2y}{dx^2} + (L-Mx^2+Nx^4)y=0. \quad . \quad . \quad (24)$$

Now the last coefficient may be written

$$L(1-x^2) + (L+N-M)x^2 + Nx^2(x^2-1),$$

so that (24) may be written

$$\frac{d^2y}{dx^2} + \left\{ \frac{L}{x^2(1-x^2)} - \frac{\mathcal{A}-1}{(1-x^2)^2} - \frac{N}{1-x^2} \right\} y = 0. \quad (25)$$

Change  $x$  into  $\sin x$ , then (25) becomes

$$\frac{d^2y}{dx^2} + \tan x \frac{dy}{dx} + Qy = 0, \quad . \quad . \quad . \quad (26)$$

where

$$Q = \frac{L}{\sin^2 x} - \frac{\mathcal{A}-1}{\cos^2 x} - N.$$

Taking the criticoid of (26), we obtain

$$\frac{d^2y}{dx^2} + Ry = 0,$$

where, after due substitutions,

$$R = L - N - \mathcal{A}^2 + \frac{1}{2} + L \cot^2 x - (\mathcal{A}^2 - \frac{1}{4}) \tan^2 x = L \cot^2 x + m + 1 + n \tan^2 x, \text{ suppose.}$$

The last differential equation will be solved regularly if  $\mathcal{A}$  be an integer, and if  $\mathcal{A}^2 - \frac{1}{4} = j(j+1)$ , where  $j$  is an integer, *i. e.* if  $\mathcal{A}$  is half an odd integer. Hence a primary form will have become regular. Again, let

$$\mathcal{A}^2 = m - L - n + 1 = \frac{1}{4} - N = (E + \frac{1}{2})^2;$$

then, if  $E$  be an integer,  $2\mathcal{A}$  will be half an odd integer, and,  $\mathcal{A}$  being entire, a regular form will have become primary.

14. If in (25) we change  $x$  into  $\sec x$  and take the criticoid, we obtain a result in which the above value of  $R$  is replaced by

$$R = N - L - \mathcal{A}^2 + \frac{1}{2} - (\mathcal{A}^2 - \frac{1}{4}) \cot^2 x + N \tan^2 x = \lambda \cot^2 x + \mu + 1 + N \tan^2 x, \text{ suppose.}$$

Here

$$\mathcal{A}^2 = \mu - \lambda - N + 1 = \frac{1}{4} - L = (A - \frac{1}{2})^2,$$

and corresponding inferences may be drawn.

15. The theory of coresolvents shows that if in (10) we take

$$z = \frac{1}{2} \left\{ \frac{1}{\sqrt{3}} - (\tan \frac{1}{2} am x)^2 \right\}^2,$$

where the modulus of the elliptic integral is  $\cos 15^\circ$ , then, if  $a=0$ , the equation is soluble\*. If we rationalize it by changing  $x$  into  $\cos am x$ , it becomes

$$(1-x^2) \{1-c^2(1-x^2)\} \frac{d^2y}{dx^2} + P \frac{dy}{dx} + Qy = 0,$$

where

$$Q = \frac{1}{2} \left\{ \frac{1}{\sqrt{3}} - 1 + \left( \frac{1}{\sqrt{3}} + 1 \right) x \right\} \frac{1}{1+x},$$

and

$$P = x \left( \frac{c^2}{1-c^2+c^2x^2} - \frac{1}{1-x^2} \right),$$

and  $c = \cos 15^\circ$ . This form is not binomial. There is another soluble form when, with the same value of  $z$ , we have

$$\frac{1}{a} = 6z^{\frac{5}{2}} \int \frac{dx}{z^{\frac{5}{2}}},$$

the sign of integration including an arbitrary constant.

"Oakwal" near Brisbane, Queensland,  
Australia, November 20, 1874.

XVIII. *Projection of the Fraunhofer Lines of Diffraction and Prismatic Spectra on a Screen.* By Prof. JOHN C. DRAPER, *College of the City of New York*†.

HAVING been engaged during the past year in making photographs of absorption-spectra of organic bodies, in which a solar spectrum with Fraunhofer lines was formed by a diffraction-grating, I have resorted to the following method of forming such solar spectra, a description of which may prove of interest to those who are experimenting in the same field.

The grating generally used was made by Mr. L. M. Rutherford: it is ruled on speculum-metal, 6481 lines to the inch; it gives spectra by reflection. Other gratings on glass, now in my possession, give spectra by reflection and by transmission. The method answers equally well for both. It may be briefly stated as follows:—

\* See the 'Educational Times,' September 1874, p. 137, and the 'Messenger of Mathematics' there referred to.

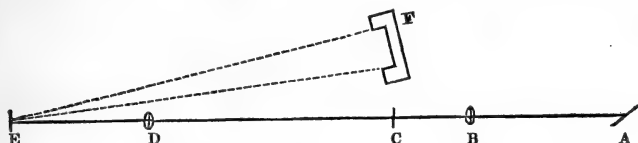
† From the American Journal of Science and Arts, vol. ix. 1875.

A beam of light is directed by the silvered plane mirror of a heliostat (A) into a darkened room.

It is received on an achromatic lens (B) 10 centims. in diameter; focal distance from posterior surface 70 centims.

A slit (C) is then placed within the focus of this lens, the distance being 48 centims. from the lens (B).

After passing through the narrow slit, which is about one tenth of a millimetre wide, the light is received upon a second achromatic lens (D), of the same diameter as the first, but with a focal



distance of 115 centims. The distance of this lens from the slit is 164 centims.; and the focusing of the lines of the spectrum on a paper screen or on the ground glass of the camera is accomplished by moving the lens (D) nearer to or further from the slit (C), or by moving the camera or screen (F) itself.

The grating (E), mounted on a suitable stand, is placed at a distance of 80 centims. from the second lens. All parts of the apparatus being carefully adjusted, so that A, B, C, D, E are on the same horizontal axis, the grating is then arranged on its vertical axis, to throw the centre of its reflected image on the opening of the slit (C).

The lines of the grating being accurately parallel to the sides of the slit, a series of beautiful spectra are produced on each side of the slit, any or all of which may be received on suitably adjusted screens, one of which is represented at F. In all of these spectra, if the slit is very narrow, the prominent Fraunhofer, with numerous other lines, appear sharply defined.

Of the spectra described above, only the first, second, and third orders on each side of the image of the slit are available for general use, on account of the overlapping of those that follow. Of those that are available, I have preferred to use the second order, since in this the dispersion is much greater than in the first, and by the apparatus described above a spectrum of a length of more than 30 centims. is obtained.

For the projection of the prismatic spectrum a prism is substituted in place of the grating, when a very fine spectrum is produced, the focus of the violet end of which is very much closer to the prism than that of the red end.

In the diffraction-spectra, also, it is necessary to vary the angle at which the screen is placed to define sharply the lines at the

extremities of each spectrum. In the spectra of the first order on each side, the screen is placed very nearly at right angles to a line drawn from the grating to B in the spectrum. As each order in succession is examined, the divergence from this angle is greater and greater, and at the same time the focal distance of the lines moves nearer to the grating.

The lenses I have employed were those of a very fine photographic combination; they give with the rest of the arrangement a spectrum in which the definition of the lines is perfect, and they are present by hundreds. Though the lenses are 10 centims. in diameter, only the central portion of each is used, a diaphragm with a circular aperture of 5 centims. or less being placed in front of B.

To form the absorbent spectra of any organic substance, a suitable solution of the same is poured into a cell with parallel sides. This is placed at any convenient point between A and B, care being taken that the faces of the cell are at right angles to the course of the ray A, B. The slit may in this case be opened wider, when each spectrum will show the characteristic absorbent bands of the substance employed, the position being indicated (and, if required, recorded) by their relation to the lines of the solar spectrum in which they are produced.

When the calcium or electric light is to be used for lecture-room demonstration of diffraction-spectra, the lens (B) should have as short a focus and as large a diameter as possible. The grating may also be so arranged on its vertical axis as to throw its image at a right angle to the line B E, to be there received on a screen. Though by this device the spectra on one side of the image of the grating are greatly elongated, and those on the other compressed, it presents the advantage of enabling the audience to see all the spectra at once, and also the optical contrivances by which they are produced.

### XIX. *Proceedings of Learned Societies.*

#### ROYAL SOCIETY.

[Continued from vol. xlviii. p. 541.]

May 7, 1874.—William Spottiswoode, M.A., Treasurer and Vice-President, in the Chair.

THE following communication was read :—

Addition to the Paper, "Volcanic Energy: an attempt to develop its true Origin and Cosmical Relations"\*. By Robert Mallet, A.M., C.E., F.R.S., M.R.I.A., &c.

Referring to his original paper (Phil. Trans. 1873), the author

\* Phil. Mag. vol. xlv. p. 468.

remarks here that, upon the basis of the heat annually dissipated from our globe being equal to that evolved by the melting of 777 cubic miles of ice at zero to water at the same temperature, and of the experimental data contained in his paper, he had demonstrated, in terms of mean crushed rock, the annual supply of heat derivable from the transformation of the mechanical work of contraction available for volcanic energy, and had also estimated the proportion of that amount of heat necessary to support the annual vulcanicity now active on our globe; but, from the want of necessary data, he had refrained from making any calculation as to what amount in volume of the solid shell of our earth *must* be crushed annually, in order to admit of the shell following down after the more rapidly contracting nucleus. This calculation he now makes upon the basis of certain allowable suppositions, where the want of data requires such to be made, and for assumed thicknesses of solid shell of 100, 200, 400, and 800 miles respectively.

From the curve of total contraction (plate x. *Phil. Trans.* part i. 1873) obtained by his experiments on the contraction of slags, he has now deduced partial mean coefficients of contraction for a reduction in temperature of  $1^{\circ}$  Fahr., for intervals generally of about  $500^{\circ}$  for the entire scale, between a temperature somewhat exceeding that of the blast-furnace and that of the atmosphere, or  $53^{\circ}$  Fahr. And applying the higher of these coefficients to the data of his former paper, and to the suppositions of the present, he has obtained the absolute contraction in volume of the nuclei appertaining to the respective thicknesses of solid shell above stated. In order that the shell may follow down and remain in contact with the contracted nucleus, either its thickness must be increased, its volume remaining constant, or the thickness being constant, a portion of the volume must be extruded. The former supposition is not admissible, as the epoch of mountain-building has apparently ceased; adopting the second, the author calculates the volume of matter that must be crushed and extruded from the shell in order that it may remain in contact with the nucleus. He tabulates these results for the four assumed thicknesses of shell, and shows that the amount of crushed and extruded rock necessary for the heat for the support of existing volcanic action is supplied by that extruded from the shell of between 600 and 800 miles thickness, and that the volume of material, heated or molten, annually blown out from all existing volcanic cones, as estimated in his former paper, could be supplied by the extruded matter from a shell of between 200 and 400 miles in thickness.

On data which seem tolerably reliable the author has further been enabled to calculate, as he believes for the first time, the actual amount of annual contraction of our globe, and to show that if that be assumed constant for the last 5000 years, it would amount to a little more than a reduction of about 3.5 inches on the earth's mean radius. This quantity, mighty as are the effects it produces as the efficient cause of volcanic action, is thus shown to be so small as to elude all direct astronomical observation, and,

when viewed in reference to the increase of density due to refrigeration of the material of the shell, to be incapable of producing, during the last 2000 years, any sensible effect upon the length of the day. The author draws various other conclusions, showing the support given by the principal results of this entirely independent investigation to the verisimilitude of the views contained in his previous memoir.

May 21.—William Spottiswoode, M.A., Treasurer and Vice-President, followed by Dr. Sharpey, Vice-President, in the Chair.

The following communications were read :—

“On Combination of Colour by means of Polarized Light.” By W. Spottiswoode, M.A., Treas. and V.P.R.S.

The results of combining two or more colours of the spectrum have been studied by Helmholtz, Clerk Maxwell, Lord Rayleigh, and others; and the combinations have been effected sometimes by causing two spectra at right angles to one another to overlap, and sometimes by bringing images of various parts of a spectrum simultaneously upon the retina. Latterly also W. v. Bezold has successfully applied the method of binocular combination to the same problem (Poggendorff, *Jubelband*, p. 585). Some effects, approximating more or less to these, may be produced by chromatic polarization.

*Complementary Colours.*—First, as regards complementary colours. If we use a Nicol's prism, N, as polarizer, a plate of quartz, Q, cut perpendicularly to the axis, and a double-image prism, P, as analyzer, we shall, as is well known, obtain two images whose colours are complementary. If we analyze these images with a prism, we shall find, when the quartz is of suitable thickness, that each spectrum contains a dark band, indicating the extinction of a certain narrow portion of its length; these bands will simultaneously shift their position when the Nicol N is turned round. Now, since the colours remaining in each spectrum are complementary to those in the other, and the portion of the spectrum extinguished in each is complementary to that which remains, it follows that the portion extinguished in one spectrum is complementary to that extinguished in the other; and in order to determine what portion of the spectrum is complementary, the portion suppressed by a band in any position we please, we have only to turn the Nicol N until the band in one spectrum occupies the position in question, and then to observe the position of the band in the other spectrum. The combinations considered in former experiments are those of simple colours; the present combinations are those of mixed tints, viz. of the parts of the spectrum suppressed in the bands. But the mixture consists of a prevailing colour, corresponding to the centre of the band, together with a slight admixture of the spectral colours immediately adjacent to it on each side.

The following results, given by Helmholtz, may be approximately verified :—

Complementary Colours.

Red,	Green-blue ;
Orange,	Cyanic blue ;
Yellow,	Indigo-blue.
Yellow-green,	Violet.

When in one spectrum the band enters the green, in the other a band will be seen on the outer margin of the red and a second at the opposite end of the violet—showing that to the green there does not correspond one complementary colour, but a mixture of violet and red, *i. e.* a reddish purple.

*Combination of two Colours.*—Next as to the combination of two parts of the spectrum, or of the tints which represent those parts. If, in addition to the apparatus described above, we use a second quartz plate, *Q*, and a second double-image prism, *P*<sub>1</sub>, we shall form four images, say *OO*, *OE*, *EO*, *EE*; and if *A*, *A'* be the complementary tints extinguished by the first combination *QP* alone, and *B*, *B'* those extinguished by the second *Q*<sub>1</sub> *P*<sub>1</sub> alone, then it will be found that the following pairs of tints are extinguished in the various images:—

Image.	Tints extinguished.
<i>OO</i>	<i>B, A</i> ,
<i>OE</i>	<i>B', A'</i> ,
<i>EO</i>	<i>B', A</i> ,
<i>EE</i>	<i>B, A'</i> .

It is to be noticed that in the image *OE* the combination *Q*<sub>1</sub> *P*<sub>1</sub> has extinguished the tint *B'* instead of *B*, because the vibrations in the image *E* were perpendicular to those in the image *O* formed by the combination *QP*. A similar remark applies to the image *EE*.

The total number of tints which can be produced by this double combination *QP*, *Q*<sub>1</sub> *P*<sub>1</sub> is as follows:—

- 4 single images,
- 6 overlaps of two,
- 4 overlaps of three,
- 1 overlap of four.

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Total. . 15

*Collateral Combinations.*—The tints extinguished in the overlap *OO*+*EO* will be *B*, *A*, *B'*, *A'*; but since *B* and *B'* are complementary, their suppression will not affect the resulting tint except as to intensity, and the overlap will be effectively deprived of *A* alone; in other words, it will be of the same tint as the image *O* would be if the combination *Q*<sub>1</sub> *P*<sub>1</sub> were removed. Similarly the overlap *OE*+*EE* will be deprived effectually of *A'* alone; in other words, it will be of the same tint as *E*, if *Q*<sub>1</sub> *P*<sub>1</sub> were removed. If therefore

the Nicol N be turned round, these two overlaps will behave in respect of colour exactly as did the images O and E when Q P was alone used. We may, in fact, form a Table thus :—

Image.	Colours extinguished.
OO+EO	$B + A + B' + A = B + B' + A = A$
OE+EE	$B' + A' + B + A' = B + B' + A' = A'$

And since the tints B, B' have disappeared from each of these formulæ, it follows that the second analyzer P may be turned round in any direction without altering the tints of the overlaps in question.

In like manner we may form the Table

OO+EE	$B + A + B + A' = B + A + A' = B$
OE+EO	$B' + A' + B' + A = B' + A + A' = B'$

Hence if the Nicol N be turned round, these overlaps will retain their tints; while if the analyzer P<sub>1</sub> be turned, their tints will vary, although always remaining complementary to one another.

There remains the other pair of overlaps, viz. :—

OO+OE	$B + A + B' + A'$
EO+EE	$B' + A + B + A'$

Each of these is deprived of the pair of complementaries A, A', B, B'; and therefore each, as it would seem, ought to appear white of low illumination, *i. e.* grey. This effect, however, is partially masked by the fact that the dark bands are not sharply defined like the Fraunhofer lines, but have a core of minimum or zero illumination, and are shaded off gradually on either side until at a short distance from the core the colours appear in their full intensity. Suppose, for instance, that B' and A' were bright tints, the tint resulting from their suppression would be bright; on the other hand, the complementary tints A and B would be generally dim, and the image B+A bright, and the overlap B+A+B'+A' would have as its predominating tint that of B+A; and similarly in other cases.

There are two cases worth remarking in detail, viz., first, that in which

$$B=A', B'=A,$$

*i. e.* when the same tints are extinguished by the combination Q P and by Q<sub>1</sub> P<sub>1</sub>. This may be verified by either using two similar quartz plates Q<sub>1</sub> Q<sub>1</sub>, or by so turning the prism P<sub>1</sub> that the combination Q<sub>1</sub> P<sub>1</sub> used alone shall give the same complementary tints as Q P when used alone. In this case the images have for their formulæ the following :—

OO	OEO	EO	EE
A+A'	A+A'	2A	2A';

in other words, OO and EO will show similar tints, and EO, EE complementary. A similar result will ensue if B=A, B'=A'.



Again, even when neither of the foregoing conditions is fulfilled, we may still, owing to the breadth of the interference-bands, have such an effect produced that sensibly to the eye

$$B + A = B' + A' ;$$

and in that case

$$\begin{aligned} B' + A &= B + A - A' + A \\ &= B + A' + 2A - 2A', \end{aligned}$$

which imply that the images O O and O E may have the same tint, but that E O and E E need not on that account be complementary. They will differ in tint in this, that E E, having lost the same tints as E O, will have lost also the tint A, and will have received besides the addition of two measures of the tint A'.

*Effect of Combinations of two Colours.*—A similar train of reasoning might be applied to the triple overlaps. But the main interest of these parts of the figure consists in this, that each of the triple overlaps is complementary to the fourth single image, since the recombination of all four must reproduce white light: hence the tint of each triple overlap is the same to the eye as the mixture of the two tints suppressed in the remaining image; and since by suitably turning the Nicol N or the prism P<sub>1</sub>, or both, we can give any required position to the two bands of extinction, we have the means of exhibiting to the eye the result of the mixture of the tints due to any two bands at pleasure.

*Effect of Combinations of three Colours.*—A further step may be made in the combination of colours by using a third quartz, Q<sub>2</sub>, and a third double-image prism, P<sub>2</sub>, which will give rise to eight images; and if C C' be the complementaries extinguished by the combination Q<sub>2</sub> P<sub>2</sub>, the formulæ for the eight images may be thus written:—

OOO	C + B + A.
OOE	C + B' + A'.
OEO	C' + B' + A.
OEE	C' + B + A'.
EOO	C' + B + A.
EOE	C' + B' + A'.
EEO	C + B' + A.
EEE	C + B + A'.

The total number of combinations of tint given by the compartments of the complete figure will be:—

$\frac{8}{1}$	=	8	single images.
$\frac{8.7}{1.2}$	=	28	overlaps of two.
$\frac{8.7.6}{1.2.3}$	=	56	„ three.
$\frac{8.7.6.5}{1.2.3.4}$	=	70	„ four.
$\frac{8.7.6}{1.2.3}$	=	56	„ five.
$\frac{8.7}{1.2}$	=	28	„ six.
$\frac{8}{1}$	=	8	„ seven.
1	=	1	„ eight.
Total		255	

The most interesting features of the figure consist in this, that the subjoined pairs are complementary to one another, viz. :—

OOO	EOE
C + B + A	C' + B' + A'
EOO	OOE
C' + B + A	C + B' + A
EEO	OEE
C + B' + A	C' + B + A'
EEE	OEO
C + B + A'	C' + B' + A

And if the prisms P, P<sub>1</sub>, P<sub>2</sub> are so arranged that the separations due to them respectively are directed parallel to the sides of an equilateral triangle, the images will be disposed thus :—

	OEO	OOO	
EEO	EEO	OEE	OOE
	EEE	OEO	

The complementary pairs can then be read off, two horizontally and two vertically, by taking alternate pairs, one in each of the two vertical, and two in the one horizontal row; and each image will then represent the mixture of the three tints suppressed in the complementary image.

*Low-tint Colours.*—A slight modification of the arrangement above described furnishes an illustration of the conclusions stated

by Helmholtz, viz. that the low-tint colours (*couleurs dégradées*), such as russet, brown, olive-green, peacock-blue, &c., are the result of relatively low illumination. He mentioned that he obtained these effects by diminishing the intensity of the light in the colours to be examined, and by, at the same time, maintaining a brilliantly illuminated patch in an adjoining part of the field of view. If therefore we use the combination N, Q, P,  $P_1$  (*i. e.* if we remove the second quartz plate), we can, by turning the prism P round, diminish to any required extent the intensity of the light in one pair of the complementary images, and at the same time increase that in the other pair. This is equivalent to the conditions of Helmholtz's experiments; and the tints in question will be found to be produced.

“Further Experiments on the Transmission of Sound.” By John Tyndall, D.C.L., LL.D., F.R.S., &c.

The author describes a number of experiments made with heterogeneous atmospheres obtained by saturating alternate layers of air with the vapours of various volatile liquids. Starting from his observation on the transmission of sound through a snow-storm on the Mer de Glace, in the winter of 1859, he shows the extraordinary power of sound to pass through the interstices of solid bodies as long as the continuity of the air is preserved. Sound, for example, penetrates through twelve layers of a silk handkerchief, while a single layer of the same handkerchief dipped into water, so as to fill the interstices, cuts off the sound.

He also describes numerous experiments with artificial fogs of a density so great that a depth of three feet sufficed to intercept the concentrated beam of the electric light; the effect of such fogs on sound was sensibly *nil*. Experiments were also executed on the illumination of such fogs by sudden flashes, obtained by the combustion of gunpowder or gun-cotton, or by the alternate extinction and revival of the electric and other lights. Such flashes promise to be extremely useful as fog-signals.

The author corrects the mistake of supposing that, in the experiments at the South Foreland, the lower trumpets were not compared with the higher ones. This, in fact, was the first step of the inquiry.

He also communicated an extraordinary instance of the interception of sound during one of the battles of the late American war.

In these experiments the author has been ably aided by his assistant, Mr. John Cottrell. An account of the experiments will be found in a paper now printing for the Philosophical Transactions.

## GEOLOGICAL SOCIETY.

[Continued from p. 77.]

February 25, 1874.—John Evans, Esq., F.R.S., President, in the Chair.

The following communication was read:—

“Note on the occurrence of Sapphires and Rubies *in situ* with Corundum, at the Culsagee Corundum Mines, Macon Co., North Carolina.” By Col. C. W. Jenks.

The mine described in this paper is in a hill situated about nine miles east of Franklin, the chief town of Macon County, rising about 400 feet above the valley. The hill is a boss of serpentine protruded through the surrounding granite. The corundum occurs in five nearly parallel veins, cropping out for about a mile along the steep side of the hill in a direction N.E. and S.W. The veins all dip to the S.E. about 45°. They are thin at the surface, but widen out as they descend, the thickness of the vein in the deepest working (75 feet) being about 10 feet. They consist of a mass of chlorite, Jefferisite, and corundum, the latter forming from one third to one half of the mass, and occurring in crystals imbedded in the other minerals. The author gives a list of several minerals which also occur in the veins, including two new silicates, which Prof. Genth has called Kerrite and Maconite. Analyses of some of these minerals and of the serpentine rock are appended to the paper. Some of the crystals of corundum weigh as much as 300 pounds. The corundum is crushed and used for grinding and polishing stones, glass, and metal; about 200 tons have been extracted from the mine. The colour of the crystals is very variable; and some of them show different colours in different parts. Many rubies and sapphires have been already procured and cut for setting.

March 11th, 1874.—John Evans, Esq., F.R.S., President, in the Chair.

The following communications were read:—

1. “On the relationship existing between the *Echinothuridæ*, Wyville Thomson, and the *Perischoechinidæ*, McCoy.” By R. Etheridge, Esq., jun., F.G.S.

In this paper the author referred in the first place to the peculiar characters of the genera *Calveria* and *Phormosoma*, Wyville Thomson, and especially to those in which they approach the Cretaceous genus *Echinothuria*, S. P. Woodward, and which led Prof. Wyville Thomson to include these three forms in his group *Echinothuridæ*. He remarked that an overlapping of the interambulacral plates, more or less like that occurring in these three genera, is met with also in *Archæocidaris*, McCoy, and *Lepidechinus*, Hall, belonging to the group of palæozoic Echini which McCoy proposed to call *Perischoechinidæ*, and which is characterized by the presence of more than three rows of plates in the interambulacral areas. As

there is no overlapping of these plates in the other genera referred to this group, it includes two types of structure. The author then discussed the characters presented by the test in the genera of the Perischoechinidæ (namely *Archæocidaris*, *Palæchinus*, *Perischodomus*, *Lepidechinus*, *Eocidaris*, *Melonites*, and *Oligoporus*), and pointed out that although we have no conclusive evidence of the presence of membranous interspaces along with the overlapping plates in *Archæocidaris*, the fragmentary condition in which the remains of that form are usually found would lead us to infer their existence. No known palæozoic genus exhibits the want of distinction between the ambulacra and interambulacra on the ventral half of the test seen in the recent genus *Phormosoma*. In *Melonites* and *Oligoporus* the author described an increase in the number of rows of plates in the ambulacra, and he indicated that all the Perischoechinidæ differ from the later Echini by the increased number of perforations in the ocular and genital plates.

2. "On the discovery of Foraminifera &c. in the Boulder-clays of Cheshire." By William Shone, Esq., jun.

In this paper the author described the occurrence of Foraminifera, Entomostraca, and some other small organic bodies in the Boulder-clay at Newton by Chester and at Dawpool. They were found partly in the interior of specimens of *Turritella terebra*, and partly free in the Boulder-clay; but those obtained from the *Turritellæ* were in better condition than the others. The Foraminifera generally agree precisely with those found in the tidal parts of the river Dee. The author stated further that the *Turritellæ* containing Foraminifera are filled with a fine greyish-white sand, in which the minute fossils abound; and he discussed the probable conditions under which the deposit containing them had been formed.

3. "On the occurrence of a Tremadoc area near the Wrekin in South Shropshire, with description of a new Fauna." By Charles Callaway, Esq., M.A., B.Sc., &c.

The author stated that in an exposure of light-green micaceous shales dipping south-east at  $50^{\circ}$  at Shineton near Cressage, which are represented as of Caradoc age in the Geological-Survey Map, he found a series of Trilobites and other fossils which induced him to regard these Shineton shales as belonging to the Lower Tremadoc series. He described as new species *Asaphus Eos*, *Conocoryphe Salteri*, *C. angulifrons*, *Platypeltis Croftii*, *Conophrys salopiensis*, *Lichapyge cuspidata*, *Lingulella Nicholsoni*, *Metoptoma Sabrinæ*, and *Theca lineata*. The author regarded these shales as the equivalents of beds containing *Dictyonema* found near Malvern and at Pedwardine.

XX. *Intelligence and Miscellaneous Articles.*

ON THE EXPRESSION OF THE WORK RELATIVE TO AN ELEMENTARY TRANSFORMATION. BY J. MOUTIER.

**M.** CLAUSIUS has recently given a demonstration of Carnot's theorem, founded on the expression of the work relative to an elementary transformation on the hypothesis now generally admitted, in which heat is considered to be a mode of motion. M. Ledieu arrived at the same result by a different path. These solutions leave the nature of the motion undetermined, and by that very fact present the greatest generality. My intention is to treat the same question by admitting that heat consists of a vibratory motion. The analogy existing between heat and light permits us to suppose that it is so; and as the vibration theory suffices for the explanation of all optical phenomena, there is reason to investigate whether it can likewise account for the phenomena of heat. This particular hypothesis is not new in science. It is true that it restricts the generality of the solution; but, on the other hand, it permits us to state precisely the nature of certain phenomena.

The vibratory motion with which each point is animated can be decomposed according to three rectangular directions; each component motion is an oscillatory rectilinear motion of the same period, produced by a force proportional to the distance from the material point to a fixed centre.

If we represent by  $m$  the mass of the material point, by  $\phi$  the acceleration at the unit of distance, by  $a$  the amplitude of the oscillation, the mean value of the force is  $f = \frac{1}{2}m\phi a$ .

The duration  $i$  of an oscillation is  $i = \frac{2\pi}{\sqrt{\phi}}$ .

The maximum velocity of the material point is  $U = \frac{2\pi a}{i}$ .

The maximum semi-*vis viva* is  $\frac{1}{2}mU^2 = fa$ .

The mean semi-*vis viva*  $\frac{1}{2}mu^2$  is the half of the maximum semi-*vis viva*;  $\frac{1}{2}mu^2 = \frac{1}{2}fa$ . This mean is considered to be proportional to the absolute temperature  $T$ .

The elementary work which corresponds to a rise of temperature  $dT$  is composed of two parts: one is equal to half the increment of the mean *vis viva*; the other arises from modifications brought into the vibratory motion by supposing that the mean *vis viva* preserves the same value, or else that the temperature remains constant.

The temperature remaining constant, the amplitude of the oscillation may change, provided that the duration of an oscillation varies in the same ratio. If the amplitude of the oscillation is increased by the quantity  $da$ , there results a work which is expressed by the product of the mean value of the force into the increment of the amplitude, or  $fda$ .

Now, as the ratio  $\frac{i}{a}$  is to remain constant,

$$da = \frac{a}{i} di;$$

consequently

$$fda = fa \frac{di}{i} = mv^2 \frac{di}{i}.$$

The portion of the work relative to an elementary transformation is therefore, for the motion we are considering,

$$d(\frac{1}{2}mv^2) + mv^2 \frac{di}{i}.$$

The same reasoning applies to each of the three rectangular directions in which the motion of the material point is projected. The work  $dL$ , relative to an elementary transformation, is the sum of the quantities analogous to the preceding; so that, calling  $mv^2$  the mean *vis viva* of a material point, we shall have for the entire system,

$$dL = d\Sigma(\frac{1}{2}mv^2) + \Sigma(mv^2) \frac{di}{i}.$$

We thus find again the expression given by Clausius. If we represent by  $M$  the weight of the body, by  $k$  its absolute specific heat, by  $E$  the mechanical equivalent of the heat, on the hypothesis adopted concerning heat,

$$\Sigma(\frac{1}{2}mv^2) = MKTE.$$

The value of the elementary work  $dL$  can then be put under the form

$$dL = MKE \left( dT + 2T \frac{di}{i} \right).$$

Admitting, as before, that heat consists in a vibratory motion, various phenomena can be analyzed from that point of view.

1. With bodies in the solid state the ordinary specific heat is sensibly equal to three times the absolute specific heat. Let us see what indication is furnished in regard to this by the above-stated theory.

The quantity of heat necessary to increase the temperature of the body by  $dT$  is then  $3MKdT$ . A part of this heat,  $MKdT$  represents the increment of the heat really existing within the body; so that the heat expended in work is  $2MKdT$ . We have therefore

$$dT = 2T \frac{di}{i}.$$

This relation amounts to the following—

$$\frac{i^2}{T} = \text{constant}.$$

Substituting for  $i$  and  $T$  their values deduced from the preceding relations, we find the condition  $f = \text{constant}$ .

Therefore, in bodies in the solid state, when the vulgar specific heat is equal to triple the absolute specific heat, the molecular forces have a sensibly constant value, independent of the temperature. We thus rediscover a property enunciated in a previous memoir\*.

\* *Comptes Rendus*, vol. lxxi. p. 934; *Annales de Chimie et de Physique*, S. 4. vol. xxiv. p. 306.

2. Let us seek as well the condition for there being no heat consumed in internal work when the body is heated under constant volume, which is sensibly the case for permanent gases.

The quantity of heat necessary for raising the temperature by  $dT$  is then  $KdT$ ; in this case  $dL=0$ ,

$$dT + 2T \frac{di}{i} = 0.$$

This relation is equivalent to the following—

$$Ti^2 = \text{constant}.$$

By substituting for  $i$  and  $T$  the values deduced from the preceding relations we find for the condition

$$a = \text{constant}.$$

Therefore, that there may be no heat consumed in internal work when a body is heated under constant volume, the amplitude of the oscillations must remain the same; on the contrary, there is expenditure of heat in internal work when the amplitude of the oscillations increases.

3. When the body undergoes transformation with the temperature constant, as in changes of state, the quantity of heat necessary for effecting the transformation is

$$Q = 2MKT \int \frac{di}{i} = 2MKT \log \left( \frac{i}{i_0} \right),$$

designating by  $i_0$  and  $i$  the durations of an oscillation before and after the transformation, and by  $\log$  the Napierian logarithm.

The temperature being the same, if  $a_0$  and  $a$  denote the corresponding durations of an oscillation,

$$\frac{i}{i_0} = \frac{a}{a_0}.$$

But, besides,  $f_0$  and  $f$  denoting the mean values of the molecular forces before and after the transformation, the temperature remaining the same,

$$fa = f_0a_0,$$

and consequently

$$Q = 2MKT \log \left( \frac{f_0}{f} \right).$$

This relation shows the connexion existing between the heat necessary for determining a change of state, such as fusion or vaporization, and the variation of the molecular actions in consequence of the change of state. When the molecular actions diminish (which is the ordinary case), the transformation demands an expenditure of heat (heat of fusion or vaporization); while the body evolves heat when the change of state is accompanied by augmentation of the molecular forces.—*Comptes Rendus de l'Académie des Sciences*, vol. lxxx. pp. 40–44.



## ON THE ANALOGIES PRESENTED BY THE LIBERATION OF GASES FROM THEIR SUPERSATURATED SOLUTIONS AND THE DECOMPOSITION OF CERTAIN EXPLOSIVE BODIES. BY D. GERNEZ.

I established, long since\*, that, in supersaturated gaseous solutions, the excess of the quantity of gas dissolved above the normal quantity (that is, above that which the liquid would dissolve in the same conditions of temperature and pressure) does not escape, if no mechanical action be interposed, unless any gaseous atmosphere (retained, for example, at the surface of a solid body or in the capillary cavities of a porous substance) be introduced into the interior of the liquid. It is in this atmosphere, which plays the part of a vacuum in relation to the different gas dissolved, that the latter escapes at the free surface of the liquid. Now the sides of vessels often retain, even when they appear wet, a gaseous layer localized especially in the anfractuositities which are almost always found at the surface of solid bodies. Hence it results that, in vessels which have not undergone special preparation, supersaturated gaseous solutions produce in more or less abundance bubbles of gas upon the sides. But if, by washing successively with potass, boiling distilled water, and alcohol, the superficial layer of glass vessels (in certain points of which a small quantity of air is held) be carefully dissolved, we find that not a single gas-bubble will form on the side bathed by the liquid, no more than in the interior of the supersaturated solution, between very wide limits of temperature and pressure.

The emission of the gas then takes place only at the free surface of the liquid; exchanges are made from layer to layer with a slowness such that, for instance, water saturated with carbonic acid under a pressure of about  $2\frac{1}{2}$  atmospheres, and exposed in an open tube at temperatures near  $8^{\circ}$  C., is still supersaturated in the layer situated at 10 centims. from the surface, even after fifty days.

When the pressure is lessened the gas is still emitted only at the surface, if the vessel has been properly prepared. Thus water saturated with carbonic acid under a higher pressure than  $2\frac{1}{2}$  atmospheres has been very easily kept in the vacuum made with the mercury pump, without one bubble of gas being disengaged at the interior of the solution; and yet the manometer of the receiver indicated only a pressure equal to the maximum tension of aqueous vapour at the temperature of the experiment. The gas escaped only at the surface, without a bubble appearing, and with a relatively feeble velocity.

If a gaseous atmosphere be introduced into this solution at the surface of which a vacuum is maintained, a lively effervescence is produced which resembles violent ebullition. I have realized the experiment by plunging into Seltzer water a fragment of platinum-sponge or of binoxide of manganese held at the end of a platinum wire: all the liquid above the porous substance was violently projected, while below not a bubble of gas was liberated.

\* *Comptes Rendus*, Nov. 19, 1866, vol. lxiii. p. 883.

When the gas is one which is very soluble in the liquid, we can, by operating in tubes prepared as I have indicated, bring the solutions to a pressure sufficiently feeble, or to a temperature high enough, for the quantity of gas held by the liquid to be very considerably more than the normal quantity. If a gaseous atmosphere be then introduced to the interior of the liquid, a sort of ebullition will be determined. The experiment can very readily be realized with ammonia solution. The ordinary solution is put into a prepared tube, surrounded with a freezing-mixture, and is saturated by passing for a long time a current of gaseous ammonia. The tube containing the solution is then taken out and allowed to return to the surrounding temperature, say, of  $20^{\circ}\text{C}.$ ; no gas is liberated within the liquid; but if the end of a glass tube, formed at the lamp into a small bell, containing air be put into it, ammonia gas escapes in that atmosphere, and seems to issue from the bell, in bubbles the more frequent the more pronounced the supersaturation. In this case the experiment resembles the ebullition excited in a liquid by the same process. Besides, when after some time it slackens, the liberation of the gas is made more active by raising the temperature a little.

In the Note above mentioned, I had already compared the phenomenon in question to the decomposition, under the same influence, of substances such as oxygenated water. The preparation of very concentrated oxygenated water being a delicate thing to execute, I will indicate how a known reaction (studied formerly by Schönbein\*) may easily be made use of for the same demonstration.

Into a glass tube from 6 to 20 millims. in diameter, closed at one end, and recently prepared as I have said above, from 5 to 10 centims. depth of distilled water is introduced, having been filtered to rid it of the solid particles held in suspension. The tube is cooled to zero; and then some liquid hyponitric acid, previously cooled, is dropped in. This liquid, gliding along the side of the tube, passes through the water without liberating any gas, and collects at the bottom of the tube in the form of a blue liquid which is regarded as containing nitrous acid; at the same time nitric acid remains in solution in the water. The tube can then be taken out of the freezing-mixture and allowed to return to the surrounding temperature, of  $15^{\circ}$  for example, without a single bubble of gas escaping from the interior of the liquid. Tubes thus prepared I have kept 15 days in a medium the temperature of which has varied from  $7^{\circ}$  to  $15^{\circ}$ : the blue liquid had been gradually diffused, without liberation of gas, in the superposed layer of water, a certain thickness of which remained colourless. If a body without chemical action upon nitric acid, and disaerated, such as a platinum wire which has been used for some minutes to maintain the ebullition of some water, be introduced to the surface of the lower layer of the liquid, it produces no effect upon it; while the other end of the wire, which has not been cleared of the adhering layer of air, is hardly brought into contact with the nitrous acid before it excites an abun-

\* Pogg. *Ann.* vol. xl. p. 382.

dant liberation of binoxide of nitrogen, which suddenly ceases if the wire be immediately withdrawn, without leaving a gas-bubble, and which recommences as soon as the wire is again immersed. At the same time the water is charged with a fresh quantity of nitric acid. This decomposition can be determined with more activity by the introduction of a little bell containing air, its outer surface having been freshly disaerated in the flame of a gas-burner. The bubbles of binoxide then seem to issue from the bell, as in the solution of ammonia. This effect, of a gaseous atmosphere decomposing nitrous acid, can be observed even at the temperature of zero (Centigrade); in this case the liberation of the binoxide of nitrogen is less rapid.

There is, then, the closest analogy between the emission of a dissolved gas, effected at the surface of the solution, into a gaseous medium as into a rarefied atmosphere, and that decomposition of explosive bodies which, as I have pointed out in the case of oxygenated water, there is no reason to attribute to a peculiar catalytic force. Moreover the evolution of heat which accompanies the decomposition of these bodies, though slight in the case of nitrous acid, explains the rapidity with which the phenomenon proceeds as soon as it has been induced at one point of the body, unless the reaction be arrested at its starting, as I have here shown.—*Comptes Rendus de l'Acad. des Sciences*, Jan. 4, 1875, pp. 44–47.

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ON VENUS AS A LUMINOUS RING. BY PROF. C. S. LYMAN.

In this Journal\*, eight years ago, a brief notice was published of some observations made by the writer on Venus when near her inferior conjunction in 1866. The planet was then (for the first time, so far as appears) seen as a very delicate luminous ring. The cusps of the crescent, as the planet approached the sun, had extended gradually beyond a semicircle, until they at length coalesced and formed a perfect ring of light.

No opportunity has since occurred of repeating these observations, until the day of the recent transit. On Tuesday, December 8th, Venus was again in close proximity to the sun; and the writer had the satisfaction of watching the delicate silvery ring enclosing her disk, even when the planet was only the sun's semidiameter from his limb. This was at 4 P.M., or less than five hours before the beginning of the transit. The ring was brightest on the side towards the sun—the crescent proper. On the opposite side the thread of light was duller and of a slightly yellowish tinge. On the northern limb of the planet, some 60 or 80 degrees from the point opposite the sun, the ring for a small space was fainter and apparently narrower than elsewhere. A similar appearance, but more marked, was observed on the same limb in 1866.

These observations were made with a five-foot Clark telescope of  $4\frac{2}{3}$  inches aperture, by so placing the instrument as to have the sun cut off by a distant building while the planet was still visible.

\* Silliman's American Journal, vol. xliii. p. 129.

The ring was distinctly seen when the aperture was reduced to one and a half inch. The 9-inch equatorial could not be used, as there were no means of excluding the direct sunlight.

The morning after the transit the sky was slightly hazy, and the planet could not be found, though probably it might have been if the small telescope had been mounted equatorially.

On the day following (the 10th), the crescent, extending to more than three fourths of a circle, was seen with beautiful distinctness in the equatorial; and on this and two subsequent days, measurements were taken with the filar micrometer for the purpose of determining the extent of the cusps, and consequently the horizontal refraction of the atmosphere of the planet, on the assumption that the extension of the crescent and formation of the ring are due to this refraction.

The results of these observations are given below, each result being the mean of the number of separate measurements indicated in the last column. On the 10th, the chord of the arc between the cusps was measured; on the other days the distance between lines tangent to the cusps and to the opposite limb.

Mean dates.	Distance of centres of Sun and Venus.	Extent of Crescent.	Horizontal refraction of Venus's atm.	Number of observations of cusps.
h m				
Dec. 8... 3 0 P.M.	0 36.6	360 0		
„ 10... 11 36 A.M.	2 31.7	279 28	46.6	4
„ 11... 10 16 A.M.	4 2.5	233 15	43.0	6
„ 11... 2 40 P.M.	4 20.4	231 46	45.5	15
„ 12... 2 45 P.M.	5 58.3	215 21	42.9	22
		Mean...	44.5	

These observations give a mean of 44'.5 as the horizontal refraction of Venus's atmosphere, or about one quarter greater than that of the earth's. The writer's observations in 1866 gave 45'.3. Mädler, from observations of the cusps in 1849, when the nearest approach of the planet to the sun was 3° 26', made the refraction 43'.7.

The formula for the refraction is this :

$$\sin y = \sin d \sin \frac{c-180}{2} ; \quad 2x = y - \frac{r}{\rho},$$

in which  $d$  = distance of centres of Sun and Venus.

$c$  = arc of crescent.

$r$  = Sun's semidiameter.

$\rho$  = radius vector of Venus.

$x$  = horizontal refraction of Venus's atmosphere.

Six measurements of the diameter of the planet on the 10th give 63".1. Twenty-four on the 11th give 63".75. The English and American Almanacs give 62".4 and 64".5 respectively.—Silliman's *American Journal*, January 1875.

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XXI. *The Specific Heat of the Elements Carbon, Boron, and Silicon.*—Part I. *The Relation between the Specific Heat of these Elements in the free state and the Temperature.* By Dr. H. FRIEDRICH WEBER, *Professor of Physics and Mathematics*.\*

[With a Plate.]

DULONG and Petit in 1819 measured the specific heats of thirteen solid elements. In each case there appeared a very simple relation between the specific heat and the atomic weight: the product of the specific heat into the atomic weight was a constant quantity. The atoms of all the elements examined have therefore the same capacity for heat. If the specific heat of water be taken as the unit, and 16 as the atomic weight of oxygen, this constant (the so-called atomic heat) averages 6·0. By numerous researches, extending from 1840 to 1862, M. Regnault has shown the general applicability of this law of Dulong and Petit—the general result being that this law seems to hold good for the greater number of the solid elements, provided the specific heat of any element be determined at a temperature sufficiently under the melting-point of that element. The average atomic heat for thirty-two solid elements was 6·3, the extremes being 6·7 for sodium and 5·5 for phosphorus and sulphur. For three solid elements, however (viz. silicon, boron, and carbon), considerably smaller atomic heats were obtained—for crystallized silicon 4·8, for crystallized boron 2·7, and for crystallized car-

\* An Experimental Research presented at the fifty-sixth Anniversary of the Royal Württemberg Land- and Forest-Management Academy at Hohenheim. Translated by M. M. Pattison Muir, F.R.S.E.

bon, as diamond, so low a number as 1·8 (the atomic weights of these three elements being taken, in accordance with the results of vapour-density determinations, as 28, 11, and 12 respectively).

Silicon accordingly stands considerably without the sphere to which the law of Dulong and Petit applies; boron and carbon form unmistakable exceptions to this notably simple natural law.

The exceptional position of these three elements induced Regnault to subject their various allotropic modifications to a searching inquiry, in order to determine their specific heats. In his second communication on the specific heats of solid bodies\* he showed that the different allotropic forms of carbon are possessed of different specific heats, and that no one of these fulfils the conditions of the law of Dulong and Petit. The numbers which he gave (specific heats) are as follows:—

Animal charcoal . . .	0·2608
Wood charcoal . . .	0·2415
Coke . . . . .	0·2017
Gas-coke . . . . .	0·2036
Graphite . . . . .	0·2019
Furnace-graphite . .	0·1970
Diamond . . . . .	0·1469

In a research published in 1861, Regnault obtained analogous results for boron and silicon: the following are the specific heats of

Graphitic boron . . .	0·2352
Crystallized boron . .	0·2574
Fused silicon . . . .	0·1661
Crystallized silicon . .	0·1733

Contemporaneously with Regnault, De la Rive and Marcet examined the specific heats of two modifications of carbon by the method of cooling†. These physicists also found that the specific heat of the diamond is notably less than that of porous amorphous carbon; the specific heat of the former being given by them as 0·119, while that of the latter is 0·165. These results were an evident witness to the justice of the opinion that the physical state played as great a part as the chemical nature of the elements, as regards their specific heats, and that the law of Dulong and Petit could not, therefore, be regarded as the universal expression of the law of specific heat. De la Rive and Marcet believed that the great differences between their numbers and the numbers of Regnault could be accounted for by the fact

\* *Ann. de Chím. et de Phys.* Ser. 3. vol. i. p. 202.

† *Ibid.* Ser. 2. vol. lxxv. p. 242, and Ser. 3. vol. ii. p. 121.

that they employed a method differing from that employed by the latter physicist, and also that the substances examined could not be considered perfectly identical. Had De la Rive and Mar-  
cet examined more thoroughly into these differences, they must easily have perceived the incorrectness of their mode of account-  
ing for them (the method of cooling must give *larger*, not smaller numbers than Regnault's method of mixtures; small impurities, trivial differences in the physical state of an element, may well alter the specific heat of that element 1 per cent. or so, but surely not 30 to 60 per cent.), and that remarkable property of carbon the announcement and examination of which forms a part of the following communication would thirty years ago have most prob-  
ably been discovered.

In his comprehensive research on the specific heat of solid bodies\*, Kopp estimated anew the specific heats of carbon, boron, and silicon, using a modification of the method of mixtures; his results were as follows:—

Gas-coke . . . .	0·185	Amorphous boron	0·254	Amorphous silicon	0·214
Furnace-coke..	0·166	Crystallized boron	0·230	Fused silicon . . . .	0·138
Native graphite	0·174			Crystallized silicon	0·165

These numbers are smaller than those of Regnault. Kopp explained the different numbers obtained by using different modifications of carbon by supposing that carbon has in reality but one specific heat (that of diamond, 0·1469), and that the other varieties give higher numbers inasmuch as, being porous sub-  
stances, they absorb gases, and on coming into contact with the water of the calorimeter evolve a small quantity of heat. Kopp believed that all the allotropic modifications of each element pos-  
sess the *same* specific heat, and that variations in the number actually obtained are due to the errors of experiment, or to the use of impure materials.

Several years later (1868) Wüllner and Bettendorf attempted to show that Kopp's hypothesis was untenable, that Regnault's numbers were perfectly reliable, and that the smaller numbers obtained by Kopp did not justify the conclusion which he had drawn. The following are the numbers obtained by these authors†:—

Gas-coke . . . . .	0·2040
Native graphite . . . .	0·1955
Furnace-graphite . . . .	0·1961
Diamond . . . . .	0·1483

These numbers agree very closely with Regnault's. Wüllner

\* Liebig's *Annalen*, Ser. 3. Sup. vol. pp. i & 289.

† Pogg. *Ann.* vol. cxxxiii. p. 293.

and Bettendorf concluded that the different modifications of carbon have really different specific heats. In obtaining these numbers a small error was introduced by the following circumstance. The substance to be examined (1 to 5 grms.) was warmed in a glass with water to about  $70^{\circ}$ , and then allowed to cool to about  $20^{\circ}$  in the calorimeter. In calculating the specific heat of the substance, it was assumed that the specific heat of the water remained equal to unity throughout the experiment. Now the average specific heat of water between  $20^{\circ}$  and  $70^{\circ}$ , according to Bosscha\*, is 1.0099. Taking this number into account, Wüllner and Bettendorf's numbers become:—

Gas-coke . . . .	0.1961		Graphite .	0.1883
Furnace-graphite.	0.1861		Diamond .	0.1429

If we use the number for the specific heat of water between  $20^{\circ}$  and  $70^{\circ}$ , obtained by Jamin and Amaury†, these numbers become still smaller. We may say, then, that the numbers obtained by Wüllner and Bettendorf stand midway between those of Kopp and those of Regnault.

From a consideration of the results of all the researches upon the specific heats of carbon, boron, and silicon, it may safely be averred that the different allotropic modifications of these elements possess different specific heats, and that no one of these elements in any of its modifications obeys the law of Dulong and Petit. These three solid elementary bodies differ in this respect, therefore, from all the other elements. It is also, however, evident that the numbers obtained by the different experimenters diverge considerably from one another. The four series of determinations have not presented us with any two exactly similar numbers. The differences in the individual results are so great and so general as to preclude us from believing that they are due to errors in the methods of experiment, or to impurities in the substances themselves. Some circumstance really conditioning the specific heat of these elements, and the value of which differs in the four series of experiments, must be present.

With this idea I undertook, in the winter of 1871–72, an analysis of the estimations hitherto made of the specific heats of carbon, boron, and silicon, and arrived at the following conclusion:—*The different observers have determined the specific heats of these elements for entirely different intervals of temperature; and the greater the interval of temperature for which the specific heat is determined, the greater is the number representing that specific heat.* The following Table shows that this is the case. Column C

\* Pogg. Ann. Jubelbd. p. 545.

† Comptes Rendus, vol. lxx. p. 661.



contains the observed specific heats; the column  $\Delta T$  gives the degrees of temperature between which the experiment has been carried out.

	Regnault.		De la Rive and Marcet.		Kopp.		Wüllner and Bettendorf.	
	C.	$\Delta T$ .	C.	$\Delta T$ .	C.	$\Delta T$ .	C.	$\Delta T$ .
Wood charcoal .....	0·2415	18– 98	0·1650	6–15				
Graphite.....	0·1977	17– 99	.....	.....	0·174	21–52	0·1881	24–67
Gas-coke.....	0·2004	16–100	.....	.....	0·185	22–52	0·1960	24–69
Furnace-coke .....			.....	.....	0·166	22–52	0·1861	23–65
Diamond .....	0·1469	9– 98	0·1192	6–15	.....	.....	0·1429	24–70
Amorphous boron ...	.....	.....	.....	.....	0·254	18–48		
Graphitic boron.....	0·2352	17– 99	.....	.....				
Crystalline boron ...	0·2574	14–100	.....	.....	0·230	21–51		
Amorphous silicon...	.....	.....	.....	.....	0·214	21–51		
Fused silicon .....	0·1750	22–100	.....	.....	0·138	21–50		
Crystalline silicon ...	0·1787	21– 99	.....	.....	0·165	21–52		

From these facts I concluded that the specific heats of the different allotropic modifications of these three elements increase in an altogether surprising manner. Inasmuch as the experiments upon carbon are the most numerous and the most trustworthy, the foregoing conclusion can be most confidently applied to this element. To boron and silicon the inference cannot be applied with so much certainty. Kopp's numbers for a temperature ranging from about 20° to 50° are certainly smaller than Regnault's for the interval of temperature 20° to 100°; yet inasmuch as Kopp worked with very small quantities and with a not very exact method, it is possible that the differences arose from circumstances other than the mere difference of temperature. The analogous behaviour of carbon and boron towards Dulong and Petit's law permits us to believe that the great variability in the specific heat of the former element will find its counterpart in a like variation in the specific heat of the latter.

In an experimental inquiry into the specific heat of the diamond\*, I showed that the specific heat of this body increases, with increase of temperature, more quickly than that of any other substance; the values at 0°, 100°, and 200° were almost in the ratios 1 : 2 : 3. The number expressing the relation of the specific heat of the diamond  $y_t$  to the temperature  $t$  was calculated from the following equation:—

$$y_t = 0\cdot0947 + 0\cdot000994t - 0\cdot00000036t^2.$$

\* *Ber. der deut. chem. Ges.* 1872, p. 305; and *Pogg. Ann.* vol. cxlvii. p. 317.

Perfectly analogous results were obtained for graphite in two series of researches. From experiments made in the autumn of 1872, I concluded that the specific heat of crystalline boron increases with the temperature exactly as that of diamond and graphite increases, and that, at any rate for low temperatures, the specific heat of silicon varies with the temperature. Following up these preliminary researches, I have now for two years busied myself with an inquiry into the relation subsisting between the specific heats of the various modifications of carbon, silicon, and boron, and the temperature at which these are determined. As the investigation advanced I found that comprehensive determinations of the specific heat of these elements, as a function of the temperature, might lead to a removal of the idea that these bodies form an exception to the law of Dulong and Petit, and also to a new point of view from which to regard this law itself—that these numbers might also be useful in further determinations of the specific heat of the various modifications of any element, or of the specific heats of the elements when in chemical combination. I therefore spared no trouble in obtaining exact and trustworthy determinations of the specific heats of these elements at as many and as various temperatures as possible. Over a hundred careful measurements have been made. As regards carbon in the free state, all the problems which presented themselves have been solved; the specific heat of the different carbon-modifications has been determined for all temperatures between  $-80^{\circ}$  and  $+1000^{\circ}$ . Only in connexion with the elements boron and silicon a few questions yet remain unanswered. I prefer, however, to publish the results which I have obtained; and in the next Part I hope to correct any errors and to extend the investigation.

The greater part of this research was carried out in the Physical Institute of the University of Berlin, between December 1872 and July 1873, the remainder being conducted in the present year at Hohenheim and Stuttgart. (The author expresses his thanks to Professors Helmholtz, Rammelsberg, and G. Rose of Berlin, Tschermack of Vienna, and Marx of Stuttgart.)

### I. METHODS OF OBSERVATION.

Let  $W_1, W_2, \dots W_n$  be the amounts of heat which  $G$  weight-units of a body give up when cooled from the initial temperature  $T_1, T_2, \dots T_n$  to the final temperature  $T_0$  in a calorimeter;  $n$  different values for the specific heat of the body  $y_T$  in relation to the temperatures  $\frac{T_1 + T_0}{2}, \frac{T_2 + T_1}{2}, \dots \frac{T_n + T_{n-1}}{2}$  may be deduced (and hence what function of the temperature the specific heat represents), provided that the temperature-differences  $T_1 - T_0$ ,

$T_2 - T_1, \dots T_n - T_{n-1}$  fulfil certain conditions. Between  $y_T$  and the systems  $\left. \begin{matrix} W_1, W_2, W_3, \dots W_n \\ T_0, T_1, T_2, T_3, \dots T_n \end{matrix} \right\}$  the relations hold good:—

$$\left. \begin{aligned} W_1 &= G \int_{T_0}^{T_1} y_T dT, \\ W_2 &= G \int_{T_0}^{T_2} y_T dT, \\ &\dots \dots \dots \\ W_n &= G \int_{T_0}^{T_n} y_T dT. \end{aligned} \right\}$$

If the differences  $T_1 - T_0, T_2 - T_1, \dots T_n - T_{n-1}$  of the limits of integration be taken so small that the parts of the area between them are represented as trapezes, we may set down the following equations:—

$$\left. \begin{aligned} \frac{W_1}{G(T_1 - T_0)} &= y_{\frac{T_1 + T_0}{2}}, \\ \frac{W_2 - W_1}{G(T_2 - T_1)} &= y_{\frac{T_2 + T_1}{2}}, \\ &\dots \dots \dots \\ \frac{W_n - W_{n-1}}{G(T_n - T_{n-1})} &= y_{\frac{T_n + T_{n-1}}{2}}. \end{aligned} \right\}$$

How great the differences of the values  $T_0, T_1, T_2, \dots T_n$  may be taken without introducing material differences between the true values of  $y_T$  and the values as calculated depends upon the nature of the function  $y_T$ . Preliminary experiments proved that the average specific heat  $\frac{W_n - W_{n-1}}{G(T_n - T_{n-1})}$  of the elements carbon and boron within the temperature-intervals  $0^\circ$  to  $100^\circ$ ,  $100^\circ$  to  $200^\circ$ , and  $200^\circ$  to  $300^\circ$ , altered almost with the temperature. For these two elements, therefore, the temperature-differences  $T_1 - T_0, T_2 - T_1, \dots$  may rise to  $50^\circ$ . At high temperatures, between  $500^\circ$  and  $1000^\circ$ , experiment showed that the specific heat of carbon changed but very slightly as the temperature rose; within these limits, therefore, the temperature-differences may amount to  $200^\circ$ . For silicon, as the result of experiment, from  $100^\circ$  to  $200^\circ$  a temperature-difference of  $50^\circ$  was allowed; from  $0^\circ$  to  $100^\circ$  this difference must not exceed  $30^\circ$  to  $40^\circ$ .

The methods and the apparatus by means of which the values of

$$\left. \begin{array}{l} G, \\ T_0, T_1, T_2, \dots T_n, \\ W_1, W_2, W_3, \dots W_n \end{array} \right\}$$

were determined were briefly as follows:—

The *amounts by weight*,  $G$ , of the substance to be examined were determined, by means of an Ertling's balance, to within 0.1 to 0.03 per cent. of the total weight; a greater exactness was unnecessary, since the values of  $T$  and  $W$  could not be determined to within less than 0.1 per cent. of their absolute amount. The values  $T_0, T_1, T_2, \dots T_n$  and  $W_1, W_2, \dots W_n$  were not determined by the same means throughout. Within the limits  $-80^\circ$  to  $+300^\circ$  the temperature was determined directly by means of thermometers, and the corresponding quantities of heat measured by the ice-calorimeter; for high temperatures,  $500^\circ$  to  $1000^\circ$ , both of these values were calculated from the calorimeter-readings. The detailed description of both methods is as follows. As means for obtaining a range of temperature from low to high points under a red heat, solid carbon dioxide, freezing-mixtures of snow and salt, and an oil-bath were used. By regulating the gas-flame and by constantly stirring the liquid, the temperature of the oil-bath could be kept so nearly constant, that in an interval of 15 to 20 minutes it did not alter more than one degree. Two test-tubes 10 centims. long, placed one within the other, the space between them being filled with cotton-wool, formed the vessel in which the substance was heated. After the substance had been placed in this vessel, a plug of cotton-wool was inserted as a stopper, and the vessel was immersed in the cooling (or heating) liquid for a full hour. The temperature of the solid carbon dioxide and of the freezing-mixture remained during that time perfectly constant. Small variations in the temperature of the oil-bath were, as far as possible, prevented by regulating the gas-flame. At the expiry of one hour the final temperature was determined, the heating-vessel seized in the hand, removed from the bath (or cold mixture), brought into a horizontal position, and moved as quickly as possible towards the opening of the calorimeter standing close by. At the moment when the opening of the heating-vessel came very near the opening of the calorimeter the plug of cotton-wool was withdrawn, and by a quick jerk the heated substance was thrown into the calorimeter, so that without touching the walls of the instrument it should fall into the receiving vessel. After a little practice the heated substance could be deposited in the calorimeter not more than two seconds after the vessel containing it was removed from the bath. During this interval of time the

heat lost by the substance must be inappreciable, considering that it is surrounded with such bad heat-conductors (glass, air, cotton-wool, and glass). The temperature of the substance at the moment of its deposition in the calorimeter was then taken as equal to the reading of the thermometer in the bath during the five or ten minutes immediately preceding the removal of the heating-vessel. If during this time the temperature varied so much as a tenth of a degree, the mean temperature during these five or ten minutes was taken as the final temperature of the substance as it fell into the calorimeter.

All temperature-readings were reduced to the readings of the air-thermometer. The thermic expansion of the glass vessel of this thermometer, within the range  $0^{\circ}$  to  $200^{\circ}$ , was found to be

$$V_T = V_0(1 + 0.0000235T + 0.000000095T^2).$$

The constant temperatures of the solid carbon dioxide and of the snow and salt freezing-mixture were determined directly by the air-thermometer; the mean of a number of readings gave for these temperatures the values  $-79^{\circ}.5$  C. and  $-21^{\circ}.3$  C.

For temperatures between  $0^{\circ}$  and  $100^{\circ}$  two standard thermometers graduated to tenths of a degree were employed. The correction to be made in reducing the readings of these thermometers to air-thermometer readings was found to be

$$\text{For the temperature } T, \frac{0^{\circ}.13T(100-T)}{2500}.$$

For temperatures between  $100^{\circ}$  and  $300^{\circ}$  a thermometer graduated to whole degrees, but easily capable of reading to a tenth, was used. To reduce the readings of this thermometer to those of the air-thermometer the correction  $\frac{0^{\circ}.16T(100-T)}{2500}$  was ap-

plied. Every necessary correction in reading the thermometer was allowed for. In all experiments which did not involve the raising of the substances to a red heat, Bunsen's ice-calorimeter\* was used for the determination of the amounts of heat  $W_1, W_2, \dots W_n$ . Had it not been for the calorimeter of Bunsen, the following work could not have been accomplished. By means of this instrument I was able to measure with great accuracy very small amounts of heat even when using less than 1 grm. of the substance. For a description of the instrument reference must be made to Bunsen's original paper (*loc. cit.*). For calculating the amount of heat from the readings of the calorimeter I adopted the following plan.

In order to graduate the scale-tube employed, I did not use the method of employing a certain quantity of water at a known tem-

\* Pogg. *Ann.* vol. cxli. p. 1. [Phil. Mag. S. 4. vol. xli. p. 161.]

perature, inasmuch as the *exact* amount of heat,  $W_0^T$ , necessary to raise the unit weight of water from  $0^\circ$  to  $T$  is unknown. Bosscha's calculation from Regnault's results (carried out between  $100^\circ$  and  $200^\circ$ ) gives  $W_0^T = T + 0.00011T^2$ ; while Jamin and Amaury\*, for temperatures between  $0^\circ$  and  $75^\circ$ , give

$$W_0^T = T + 0.00055T^2 + 0.0000004T^3.$$

Until these anomalous results are cleared up by a new research, water must not be used for the empirical graduating of the ice-calorimeter. I have used calcspar as a standard. From the results of careful experiments made with pure substance by means of Neumann's method, the specific heat of calcspar between  $6^\circ$  and  $100^\circ$  was found to be  $0.2065$ , the specific heat of water for the temperature  $2^\circ$  to  $6^\circ$  being taken as the unit. From another series of experiments upon the changeability of the specific heat of calcspar,  $0.2061$  was deduced as the average specific heat of this substance between the points  $0^\circ$  and  $100^\circ$ . If one unit weight (one gramme) of calcspar be cooled from  $100^\circ$  to  $0^\circ$  in the ice-calorimeter,  $20.61$  heat-units are given up to the calorimeter; and the heat-unit is taken as equal to the amount of heat necessary to raise through one degree one gramme of water at a temperature between  $2^\circ$  and  $6^\circ$ . Having obtained this constant, a piece of pure calcspar weighing  $1.521$  grm., heated to a boiling heat  $T$ , was brought into the calorimeter, and the ensuing displacement of the mercury thread measured. The movement of the mercury thread corresponding to one heat-unit was then

$N_0 = \frac{N}{1.521 \cdot 0.2061 T}$ . The values of  $N_0$  for five different scale-tubes were as follows,

Scale-tube ..	A.	B.	C.	D.	E.
	millim.	millim.	millim.	millim.	millim.
$N_0 =$	14.42	10.24	9.80	6.03	4.11

referred to the mean bore of the tubes.

By careful calibration the individual bores of the tubes (600–900 millims. long) could be compared among one another; by means of the calibration Tables any actual displacement could be calculated in terms of the displacement which would have taken place had the scale-tube possessed throughout the average bore. The position of the mercury thread was read off by means of a millimetre-scale, so placed that the scale-tube covered the middle of the millimetre-marks. In reading off the position of the mercury thread the eye was placed so that the upper, under, and middle parts of the mark, seen through the tube, formed straight lines; in this way parallax was got rid off, and the readings

\* *Comptes Rendus*, vol. lxx. p. 661.

were as accurately (and much more easily) made as would have been the case had a telescope been employed. Throughout the entire research a small oscillation in the mercury thread of the calorimeter was noticed (owing to the difference of melting-point of the outer and inner ice of the instrument), varying between 0.0 millim. to 0.20 millim. per minute in winter while the calorimeter was surrounded with snow, and 0.0 millim. to 0.45 millim. per minute in summer when the calorimeter was surrounded with pure lake-ice. The correction necessary on account of this oscillation in an experiment lasting twenty or thirty minutes would be considerable; I therefore endeavoured to bring it about that the time which elapsed until the heat had been entirely spent in melting ice should be as short as possible. This time was reduced to about ten or fifteen minutes by allowing not more than 4 or 5 grms. of ice to be melted at once, and by causing the formation of a new quantity of ice by means of the introduction of a fragment of ice or snow, and the addition of a drop or two of alcohol.

In order to obviate a small loss of heat by the temperature in the receiving-vessel of the calorimeter rising above  $4^{\circ}$ , instruments of three sizes were used. For measuring quantities of heat varying from 0 to 50, from 50 to 100, and from 100 to 200 heat-units, the receiving-vessel of the instrument employed was capable of containing 8, 16, and 30 grms. of water respectively. When the quantities of heat taken up by substances cooled to  $-T_0$  in rising to  $0^{\circ}$  had to be determined by means of the *formation* of a corresponding amount of ice, alcohol was used instead of water in the receiving-vessel, care being taken that the proximity of these cold bodies did not bring the temperature of the snow or ice-film in the calorimeter beneath its melting-point.

For the measurement of such high temperatures as  $500^{\circ}$ – $1000^{\circ}$ , as I could not readily obtain a suitable air-thermometer, I made use of the device to be described. This method may not yield such altogether accurate results as those of the air-thermometer; yet it is suited for solving, in a measure at all events, all the problems connected with the specific heat of elements at high temperatures. Supposing that the amount of heat necessary to raise a unit weight of platinum from the temperature  $T_0$  to the high temperature  $T$  (measured by the air-thermometer) has been determined by carefully conducted experiments, and is expressed by the function  $\Pi(T-T_0)$ , then it is possible to calculate the temperature  $T$  by determining the amount of heat,  $W_{T_0}^T$ , given up by the unit weight of platinum in cooling, in the calorimeter, from the unknown temperature  $T$  to the known final tempera-

ture  $T_0$ . It is only necessary to solve, in reference to  $T$ , the equation

$$W_{T_0}^T = \Pi(T - T_0).$$

Let  $G$  grammes of platinum and  $G'$  grammes of another substance  $K$  be raised to the same temperature  $T$ , and be then cooled to the common final temperature  $T_0$  in the same calorimeter; from the amounts of heat,  $W_P$  and  $W_K$ , given out by the substances in cooling, it is possible to calculate the temperature  $T$  to which both substances were heated, and also the average specific heat,  $C_{T_0-T}$ , between the temperatures  $T$  and  $T_0$  of the substance by solving the equations

$$W_P = G \cdot \Pi(T - T_0),$$

from which  $T - T_0$  may be deduced, and

$$\frac{W_K}{G'(T - T_0)} = C_{T_0-T}.$$

Pouillet\* has carefully determined the amount of heat required to raise a unit weight of platinum from  $T_0$  to  $T$  where  $T_0 = 0^\circ$  and  $T = 1200^\circ$ , and finds this quantity of heat,  $W_{T_0}^T$ , to be the following function of the temperature—

$$W_{T_0}^T = 0.03237(T - T_0) + 0.0000041(T^2 - T_0^2).$$

As the estimation was made with all care, I adopted it as the basis for my determination of specific heats at high temperatures. The recent researches of Deville and Troost, which show that platinum at high temperature is permeable by gases, and that the air in the air-thermometer used by Pouillet was therefore not entirely enclosed during his experiments, but that a slow interdiffusion of the air without and within the instrument took place through the platinum partition, have not been overlooked. Inasmuch, however, as the air without and within the thermometer was under the same circumstances of pressure and temperature, and the platinum was separated from the gaseous products of the flame employed by means of an iron muffle, any error which may be introduced must be but infinitesimal†.

Adopting, then, this determination of Pouillet's as a basis, the estimation of the specific heat of carbon at high temperatures was carried out as follows:—

\* *Comptes Rendus*, vol. iii. p. 782; and *Traité de Physique*, 6th edit. vol. i. p. 227.

† Weinhold's results (*Pogg. Ann.* vol. cxlix. p. 213) seem to be not so trustworthy as Pouillet's; he employed a very small quantity of platinum (only 9 grms.), while Pouillet used 178 grms.



Two platinum tubes, closed at their lower ends, 6 centims. in length, 1.2 centim. wide, the walls of the tubes being 1.2 millim. thick, were placed side by side at a distance of 1.2 centim., and held in this position by means of a crosspiece of platinum, from which projected perpendicularly a platinum rod by means of which the two tubes could be moved about at will.

Two pieces of platinum, of the total weight of 32.39 grms., were brought into one of the tubes; and in the other such a quantity of the substance under examination was placed as would have a heat-value nearly equal to that of the 32.39 grms. of platinum. The tubes were closed by asbestos stoppers, and placed in a small muffle made of sheet copper about 2 millims. thick, which was entirely closed and then placed at the back of the muffle of a newly constructed gas muffle-furnace, in which any temperature between 500° and 1000° could easily be obtained. From the arrangement and position of the tubes it might with safety be assumed that after the expiry of a sufficient time the contents of *both* would be at the *same* temperature. When the tubes had remained in the furnace for an hour, the perpendicular platinum rod was seized by a pair of very hot tongs and the tubes very quickly transported to a double water-calorimeter standing as close by as possible. At the proper moment, while the tubes were held in the operator's right hand, the asbestos stoppers were withdrawn simultaneously by the left hand, and the contents of the two tubes thrown, by a jerk of the right hand, the platinum into one, the carbon into the other calorimeter. After a little practice the time which elapsed from the withdrawal of the hot tubes from the furnace until the moment when the contents of the tubes found themselves in the calorimeter was reduced to 3 or at the most 4 seconds. The loss of heat during this brief time affected both tubes in an exactly similar manner, inasmuch as the tubes, in respect of size, shape, material, and temperature, were exact counterparts of one another. Considering the briefness of the time and also the thickness of the walls of the platinum tubes, the reduction in the temperature of the enclosed substances must have been extremely small. Inasmuch as the weights of the two substances were equalized so that the product of the weight into the specific heat was the same for each, the small reduction of temperature might be taken as the same in each case. Against the assumption that the temperature of the platinum was the same as that of the substance under examination at the moment when they both fell into the calorimeter, no argument of importance can be urged.

The double calorimeter employed consisted of two identical vessels of the thinnest sheet copper placed parallel to one another at a distance of 2 millims. The cover of each instrument had

two openings in it. Through one passed a thermometer, while the other, the larger of the two, served as the mouth of the calorimeter. The mouths of the two instruments were at such a distance from each other that the middle point between them coincided with the point midway between the two platinum tubes. Each calorimeter was provided with a copper stirrer; the two stirrers could, by a simple piece of mechanism, be set in motion simultaneously. The water-value of the first instrument, with thermometer and stirrer, was 3.15 grms.; the water-value of the second was 3.35 grms. Nearly the same quantity of water was used in each, in order that, by bringing into each equally heated substances whose heat-values were the same, the same rise of temperature might be obtained in each case. This was actually found to be the case, to within  $0^{\circ}.1$ , in all experiments. The thermometers used with these calorimeters were graduated to hundredths of a degree. The stirrers were set in motion 15 minutes before each trial, the alteration of temperature being noted every five minutes in each instrument. Both calorimeters showed always the same change of temperature, this change never amounting to more than  $\pm 0^{\circ}.006$  per minute. The temperature was noted immediately before the heated substances were thrown in; as the substance touched the water, no development of vapour was noticed in any case, nor could even the slightest sound be heard indicative of the escape of gas-bubbles.

The stirrers were kept in operation until fully ten minutes had elapsed from the time when the heated substances fell into the calorimeters, the temperature of each instrument being read off minute by minute, in order that the fall of temperature per minute might be obtained. The maximum of temperature always occurred before the expiry of the first minute, after which the temperature very steadily sunk. The temperature at the end of the second minute was taken as the definite final temperature; and to this was added the correction  $\Delta = \frac{1}{2}(\Delta\Theta + 3\Delta\Theta')$ , where  $\Delta\Theta$  and  $\Delta\Theta'$  represent the temperature-alterations per minute before and after the heated substance was thrown into the calorimeter. This correction never reached 2 per cent. of the temperature-increase  $\Delta t$  of the calorimeter.

If  $G_p$  and  $G_k$  represent the weights of platinum and of the other substance, K, used,  $Q_p$  and  $Q_k$  the water-values,  $\Delta t_p$  and  $\Delta t_k$  the rise of temperature, and  $t_p$  and  $t_k$  the corrected final temperatures in the respective calorimeters, then the common initial temperature of the platinum and of the substance K, and also the average specific heat,  $C_{t_k-T}$ , of the substance K may be obtained by solving the two equations

$$\frac{Q_p \cdot \Delta t_p}{G_p} = 0.03232(T - t_p) + 0.0000041(T_2 - t_p^2), \quad (1)$$

and

$$\frac{Q_k \cdot \Delta t_k}{G_k} = C_{t_k - T}(T - t_k). \quad (2)$$

It were an impossible request to demand for experiments such as these, made at temperatures so high, an accuracy equal to that which attaches to measurements conducted at low temperatures; sources of error will unavoidably creep in. If by more exact researches Pouillet's expression

$$W_{T_0}^T = 0.03237(T - T_0) + 0.0000041(T^2 - T_0^2)$$

be found not wholly correct, this will but slightly alter the results of the experiments described in the present paper. The numerical value attaching to the specific heat of carbon at high temperatures may be somewhat modified; yet the general result, that the two modifications of carbon have for about 600° an almost identical specific heat, will remain unchanged.

## II. THE SPECIFIC HEAT OF CARBON.

### A. *Specific Heat of Diamond.*

In my former estimation of the specific heat of diamond\* I made use of two clear crystals belonging to the Berlin Mineralogical Museum, of the total weight of 1.061 grm. When this small weight of substance was heated 20° or 30° and brought into the ice-calorimeter, the mercury thread receded not more than 20 to 40 divisions of the scale-tube. From further experiments I found that the mercury thread is never moved to the exact point corresponding to the amount of heat developed in the calorimeter, but that it always stops a little before reaching this point. If, then, the total displacement of the mercury-thread be small, this error in the proper position of the thread will cause the results calculated therefrom to be too low. On this account my former determinations of the specific heat of diamond from 0° to 30° were too small. In order to reduce this error to the smallest possible limits, the only plan was to use a larger amount of diamond. Through the kindness of the late Prof. G. Rose, the entire diamond collection belonging to the Berlin University was placed at my disposal. I selected the following stones:—

\* *Ber. der deut. chem. Ges.* vol. iv.; and *Pogg. Ann.* 1872, part ii.

A. Clear	. . .	48-sided, weighing	446 milligrms.
B. „	. . .	24-sided, „	615 „
C. „	. . .	24-sided, „	357 „
D. Brownish	. .	8-sided, „	402 „
E. Greenish yellow		8-sided, „	345 „
F. Transparent	. spherical,	„	1397 „

The total weight was therefore 3·562 grms.

The thermic relations of these six specimens were not altogether identical. From a number of determinations, the average specific heats for the temperatures  $0^{\circ}$  to  $100^{\circ}$  were deduced as follows :—

$$\left. \begin{array}{l} A + B + C = 0\cdot1438 \\ D + E = 0\cdot1451 \\ F = 0\cdot1485 \end{array} \right\}$$

The evidently not perfectly homogeneous masses D, E, and F would therefore have been rejected had it not been for the consideration that the determination of the specific heat for the temperature-interval  $-30^{\circ}$  to  $+30^{\circ}$  could not be trusted beyond, at the furthest, the third place of decimals when working with the quantities of diamond A, B, and C only.

This degree of certainty I did not, however, deem sufficient for determining the existence of an inflection-point in the curve of the specific heat indicated by preliminary experiments. As the determination of this point appeared to me of the utmost importance, I sacrificed the advantage of working with absolutely pure material for the gain of being able to determine with the greatest possible accuracy the specific heat of the diamond at and near to the temperature  $0^{\circ}$ . In all the series of experiments the total quantity of diamond mentioned above was used.

The following Tables give the data and results of 27 experiments, having for their object the determination of the specific heat of diamond for nine different temperatures between  $-80^{\circ}$  and  $+280^{\circ}$ .

G = the weight of diamond used.

T = the temperature, measured by the air-thermometer, of the diamond at the moment when it touched the water in the calorimeter.

N = the number of divisions on the scale-tube through which the mercury thread was displaced after bringing the substance heated to T into the instrument. (The direct readings were reduced to the average bore of the tube, and then corrected for the independent oscillation of the mercury thread before the introduction of the hot substance.)

$N_0$ =the number of divisions indicating the displacement of the mercury thread when one heat-unit was developed in the calorimeter ;

$W$ =the number of heat-units, calculated from  $N$  and  $N_0$ , developed by the bringing of  $G$  grms. of the substance, heated to the temperature  $T$ , into the calorimeter ;

$C_{0-T}$ =the average specific heat between the temperature  $0^\circ$  and  $T$ , deduced from  $W$ ,  $T$ , and  $G$ ,

and

$W_{T_0}^T$ =the amount of heat required to raise a unit-weight of the substance from  $T_0$  to  $T$ .

a. *Experiments within the Temperatures  $-80^\circ$  to  $280^\circ$ , carried out by means of the Ice-calorimeter.*

First Series.

$$N_0 = 14.42.$$

G.	T.	N.	W.	$C_{0-T}$ .
3.562	-79.8	298.3	20.69	0.0728
3.562	-79.9	295.4	20.49	0.0720
3.562	-79.4	289.9	20.11	0.0711
3.562	-79.7	294.5	20.43	0.0720
$W_{-79.7}^{0.0} = 5.736.$				
Second Series.				
$N_0 = 14.42.$				
3.562	-21.35	103.9	-7.21	0.0948
3.562	-21.10	104.0	-7.21	0.0960
3.562	-21.30	104.0	-7.21	0.0951
3.562	-21.25	104.0	-7.21	0.0953
$W_{-21.2}^{0.0} = 2.024.$				
Third Series.				
$N_0 = 14.42.$				
3.562	21.20	123.3	8.55	0.1132
3.562	21.42	124.1	8.61	0.1128
3.562	21.60	124.7	8.65	0.1125
3.562	21.41	124.0	8.60	0.1128
$W_{0.0}^{21.4} = 2.414.$				

Table (*continued*).

Fourth Series.

$$N_0 = 14.42.$$

G.	T.	N.	W.	Co-T.
3.562	44.80	281.9	19.55	0.1225
3.562	45.40	287.2	19.92	0.1232
3.562	45.75	288.5	20.01	0.1228
3.562	45.35	285.9	19.83	0.1228

$$W_{0.0}^{45.35} = 5.568.$$

Fifth Series.

$$N_0 = 14.42.$$

3.562	70.45	485.4	33.66	0.1343
3.562	71.35	490.3	34.00	0.1338
3.562	71.80	492.7	34.17	0.1336
3.562	71.20	489.5	33.94	0.1339

$$W_{0.0}^{71.20} = 9.529.$$

Sixth Series.

$$N_0 = 14.42.$$

3.562	99.9	750.9	52.08	0.1463
3.562	99.9	749.4	51.97	0.1460
3.562	99.5	745.6	51.71	0.1459
3.562	99.8	748.6	51.92	0.1461

$$W_{0.0}^{99.8} = 14.576.$$

Seventh Series.

$$N_0 = 6.030.$$

3.562	179.5	694.0	115.09	0.1800
3.562	181.1	697.8	115.73	0.1794
3.562	180.0	696.5	115.51	0.1802
3.562	180.2	696.1	115.44	0.1799

$$W_{0.0}^{180.2} = 32.41.$$

Table (*continued*).

Eighth Series.

$$N_0 = 4.11.$$

G.	T.	N.	W.	C <sub>0</sub> -T.
3.562	232.4	683.5	166.31	0.2009
3.562	230.6	675.9	164.46	0.2002
3.662	233.6	684.5	166.56	0.2007
3.562	232.0	681.3	165.78	0.2006
$W_{0.0}^{232.0} = 46.57.$				
Ninth Series.				
$N_0 = 4.11.$				
3.562	280.8	898.8	218.73	0.2187
3.562	281.6	900.3	219.06	0.2184
3.562	283.6	910.8	221.59	0.2190
3.562	282.0	903.8	219.79	0.2187
$W_{0.0}^{282.0} = 61.70.$				

From average results of these nine series of experiments,

$$W_{-79.7}^{0.0} = 5.736,$$

$$W_{0.0}^{45.3} = 5.568,$$

$$W_{0.0}^{180.2} = 32.41,$$

$$W_{-21.2}^{0.0} = 2.024,$$

$$W_{0.0}^{71.20} = 9.529,$$

$$W_{0.0}^{232.0} = 46.57,$$

$$W_{0.0}^{21.4} = 2.414,$$

$$W_{0.0}^{98.8} = 14.576,$$

$$W_{0.0}^{282} = 61.70,$$

the following are deduced:—

True specific heats of the diamond $y_T$		Values of $\frac{\Delta y}{\Delta T}$
$y_{-50.5} = \frac{W_{-79.7}^{0.0} - W_{-21.2}^{0.0}}{58.5} = 0.0635$	}	0.000802 from $-50^\circ$ to $-10^\circ$ .
$y_{-10.6} = \frac{W_{-21.2}^{0.0}}{21.2} = 0.0955$		0.000812 from $-10^\circ$ to $10^\circ$ .
$y_{10.7} = \frac{W_{0.0}^{21.4}}{21.4} = 0.1128$	}	0.000837 from $10^\circ$ to $30^\circ$ .
$y_{33.4} = \frac{W_{0.0}^{45.35} - W_{0.0}^{21.4}}{23.95} = 0.1318$		0.000859 from $30^\circ$ to $60^\circ$ .
$y_{58.3} = \frac{W_{0.0}^{71.2} - W_{0.0}^{45.35}}{25.85} = 0.1532$	}	0.000856 from $60^\circ$ to $85^\circ$ .
$y_{85.5} = \frac{W_{0.0}^{99.8} - W_{0.0}^{71.2}}{28.6} = 0.1765$		0.000831 from $85^\circ$ to $140^\circ$ .
$y_{140.0} = \frac{W_0^{180.2} - W_0^{99.8}}{80.4} = 0.2218$	}	0.000779 from $140^\circ$ to $205^\circ$ .
$y_{206.1} = \frac{W_0^{232.0} - W_0^{180.2}}{51.8} = 0.2733$		0.000716 from $205^\circ$ to $250^\circ$ .
$y_{247.0} = \frac{W_0^{282.0} - W_0^{232.0}}{50} = 0.3026$	}	

From these experiments it appears that the specific heat of diamond increases uninterruptedly as the temperature increases from  $-50^\circ$  to  $+250^\circ$ ,—the velocity of this increase,  $\frac{\Delta y}{\Delta T}$ , slowly accelerating from  $-50^\circ$  to  $+60^\circ$ , and from  $+60^\circ$  to  $+250^\circ$  constantly diminishing. In the neighbourhood of  $+60^\circ$  there is a turning-point in the curve representing the specific heat of diamond. The constant diminution, from  $60^\circ$  upwards, of the value  $\frac{\Delta y}{\Delta T}$  makes it probable that this diminution will continue to increase at higher temperatures, and that there exists a temperature at which  $\frac{\Delta y}{\Delta T}$  becomes exceedingly small, or even disappears entirely—and, further, that there is a definite limit of value towards which, as the temperature rises, the specific heat tends. To test the truth of this expectation, the specific heat of the diamond was determined for three temperatures between  $500^\circ$  and  $1000^\circ$  by the aid of the double calorimeter already described. The crystals used in the foregoing experiments could not now be made use of, as at the high temperatures employed



considerable injury might be done to the costly cut diamonds. Professor Tschermack, Director of the Imperial Mineral Cabinet in Vienna, had the extreme goodness to allow me to make use of seven colourless transparent diamonds (slightly sparkling crystals, rounded pieces, and angular fragments).

In the following Tables the meanings of the letters are as follows:—

G = weight of substance employed.

Q = water-value of the calorimeter (inclusive of stirrer and thermometer).

$\Delta t$  = increase of temperature (corrected) which the calorimeter showed after the addition of the glowing substance.

W = the product of Q into  $\Delta t$ .

$\Delta T$  = the difference between the initial temperature T of the substance brought into the calorimeter and the final temperature  $T_0$  of the same substance (calculated from W and the known specific heat of platinum).

$C_{T_0-T}$  = the average specific heat for the temperature-interval  $T - T_0$ .

*b. Experiments at High Temperatures carried out by means of the double Calorimeter.*

Tenth Series.

	G.	Q.	$\Delta t$ .	W.	$\Delta T$ .	$C_{T_0-T}$ .	$T_0$ .
Platinum...	32.390	103.61	5.465	566.2	506.2	0.03454	22.25
Diamond...	3.802	105.20	5.569	580.3		0.3016	22.34
Platinum...	32.390	101.21	5.378	544.2	487.5	0.03446	22.63
Diamond...	3.802	102.30	5.471	559.8		0.3021	22.71

From the first experiments ...  $W_{22.3}^{528.5} = 152.6$ .

From the second experiments  $W_{22.7}^{510.2} = 147.2$ .

Eleventh Series.

	G.	Q.	$\Delta t$ .	W.	$\Delta T$ .	$C_{T_0-T}$ .	$T_0$ .
Platinum...	32.390	154.30	5.030	776.1	679.8	0.03524	22.04
Diamond...	3.802	165.40	5.270	872.9		0.3374	22.16
Platinum...	32.390	148.20	5.105	756.6	664.0	0.03518	22.42
Diamond...	3.790	162.85	5.223	850.5		0.3380	22.50

From the first experiments ...  $W_{22.2}^{702.0} = 229.6$ .

From the second experiments  $W_{22.5}^{686.5} = 224.4$ .

Table (continued).

## Twelfth Series.

	G.	Q.	$\Delta t$ .	W.	$\Delta T$ .	$CT_0 - T$ .	$T_0$ .
Platinum...	32.390	201.61	5.178	1043.8	892.2	0.03612	22.81
Diamond...	3.121	204.30	4.982	1017.8		0.3655	22.63
Platinum...	32.390	200.03	5.269	1054.0	900.4	0.03615	22.50
Diamond...	3.101	201.40	5.072	1021.5		0.3658	22.41
From the first experiments ... $W_{22.6}^{914.8} = 326.1$ .							
From the second experiments $W_{22.4}^{922.8} = 329.4$ .							
Thirteenth Series.							
Platinum...	32.390	241.21	5.112	1233.0	1036.7	0.03672	22.11
Diamond...	3.071	228.40	5.280	1205.9		0.3787	22.22
Platinum...	32.390	240.72	5.035	1211.9	1020.9	0.03665	22.63
Diamond...	3.036	231.21	5.048	1267.1		0.3765	22.60
From the first experiments ... $W_{22.2}^{1058.9} = 392.7$ .							
From the second experiments $W_{22.6}^{1043.5} = 384.4$ .							

With the aid of the value already obtained,  $y_{22.5} = 0.1228$ , we can reduce these eight results to a common lower limit of temperature, to the average temperature  $22^{\circ}.5$ . By this reduction the first decimals in the numerical value of  $W_{T_0}^T$  remain unchanged; we obtain:—

$$W_{22.5}^{528.5} = 152.6,$$

$$W_{22.5}^{702.0} = 229.6,$$

$$W_{22.5}^{914.8} = 326.1,$$

$$W_{22.5}^{1058.9} = 392.7,$$

$$W_{22.5}^{510.2} = 147.2,$$

$$W_{22.5}^{686.5} = 224.4,$$

$$W_{22.5}^{922.8} = 329.4,$$

$$W_{22.5}^{1043.5} = 384.4.$$

From these may be deduced:—

$$y_{615.2} = \frac{W_{22.5}^{702.0} - W_{22.5}^{528.5}}{173.5} = 0.4438,$$

$$y_{805.4} = \frac{W_{22.5}^{914.8} - W_{22.5}^{702.0}}{212.8} = 0.4535,$$

$$y_{926.9} = \frac{W_{22.5}^{1058.9} - W_{22.5}^{914.8}}{144.1} = 0.4622.$$

$$y_{598.3} = \frac{W_{22.5}^{686.5} - W_{22.5}^{510.2}}{176.3} = 0.4378,$$

$$y_{804.6} = \frac{W_{22.5}^{922.8} - W_{22.5}^{686.5}}{236.3} = 0.4444,$$

$$y_{983.1} = \frac{W_{22.5}^{1043.5} - W_{22.5}^{922.8}}{120.7} = 0.4557.$$

This calculation leads to the average value

$$y_{606.7} = \frac{1}{2} \{y_{615.2} + y_{598.3}\},$$

&c.                      &c. ;

and there results

$$y_{606.7} = 0.4408,$$

$$y_{806.5} = 0.4489,$$

$$y_{985.0} = 0.4589.$$

From these experiments it is established that the value of the increase  $\frac{\Delta y}{\Delta T}$  in the specific heat of diamond has diminished at a red heat and upwards to a white heat, until it has become but the seventeenth part of what it was for the temperature-interval  $0^\circ$  to  $100^\circ$ . This increase is now of the same magnitude as the value of  $\frac{\Delta y}{\Delta T}$  in the case of those elements which obey Dulong and Petit's law.

Further remarks and deductions will be made for graphite and diamond together, inasmuch as a value for the specific heat of graphite has been obtained almost identical with that obtained for diamond.

The curve marked diamond in the Table (Plate VII.) exhibits graphically the results of the foregoing experiments; the plain line shows the results actually observed; the notched line is interpolated from these.

[To be continued.]

## XXII. *A Statical Theorem.* By LORD RAYLEIGH, M.A., F.R.S.

[Continued from vol. xlviii. p. 456.]

SINCE the publication of the paper in the December Number of the Philosophical Magazine, entitled "A Statical Theorem," I have made some tolerably careful experimental measurements in illustration of one of the results there given, which are perhaps worth recording. The "system" consisted of a strip of plate glass 2 feet long, 1 inch broad, and about  $\frac{1}{10}$  inch in thickness, supported horizontally at its ends on two very narrow ledges. In the first experiment two points, A and B, were marked upon it, A near the centre, and B about 5 inches therefrom, for which the truth of the theorem was to be tested. When a weight W is suspended at A, the deflection in a vertical direction at B should be the same as is observed at A when W is attached at B.

The weight was suspended from a hook whose pointed extre-

nity rested on the upper surface of the bar at the marked points. In this way there was no uncertainty as to the exact point at which the weight was applied. The measurements of deflection were made with a micrometer-screw reading to the ten-thousandth of an inch, the contact of the rounded extremity of the screw with its image in the upper surface of the glass being observed with a magnifier. The reading in each position was repeated four times, with the following results.

Case 1. W hung at A. Deflection observed at B:—

W on.	W off.
79	1473
82	1473
79	1476
76	1474
Mean . . 79	Mean . . 1474

The deflection at B due to W at A was therefore 1395.

Case 2. W hung at B. Deflection observed at A:—

W on.	W off.
50	1447
47	1449
45	1445
45	1446
Mean . . 47	Mean . . 1447

Accordingly the deflection at A due to W at B was 1400.

The difference of the two deflections, amounting to only about  $\frac{1}{5}$  per cent., is quite as small as could be expected, and is almost within the limits of experimental error.

In the second experiment the test was more severe, B being replaced by another point B'  $7\frac{1}{2}$  inches distant from A, instead of only 5 inches. The deflections in the two cases here came out identical and equal to 993 divisions, W being the same as before. With W at A, the deflection at A was about 1700; and with W at B', the deflection at B' was 760.

The theorem here verified might sometimes be useful in determining the curve of deflection of a bar when loaded at any point A. Instead of observing the deflection at a number of points P, it might be simpler to measure the deflections at the fixed point A, while the load is shifted to the various points P.

For the benefit of those whose minds rebel against the vagueness of generalized coordinates, a more special proof of the theoretical result may here be given. The equation of equilibrium of a bar (whose section is not necessarily uniform) is

$$\frac{d^2}{dx^2} \left( B \frac{d^2 y}{dx^2} \right) = Y^*, \quad \dots \dots (A)$$

\* Thomson and Tait's 'Natural Philosophy,' § 617.

in which for the present application  $Y$  denotes the impressed force, *not* including the weight of the bar itself, and  $y$  is the vertical displacement due to  $Y$ .

Let  $y, y'$  denote two sets of displacements corresponding to the forces  $Y, Y'$ . Then

$$\int \left\{ y' \frac{d^2}{dx^2} \left( B \frac{d^2 y}{dx^2} \right) - y \frac{d^2}{dx^2} \left( B \frac{d^2 y'}{dx^2} \right) \right\} dx = \int \{ y' Y - y Y' \} dx, \quad (B)$$

where the integration extends over the whole length of the bar. Now, integrating by parts,

$$\int y' \frac{d^2}{dx^2} \left( B \frac{d^2 y}{dx^2} \right) dx = y' \frac{d}{dx} \left( B \frac{d^2 y}{dx^2} \right) - \frac{dy'}{dx} B \frac{d^2 y}{dx^2} + \int B \frac{d^2 y}{dx^2} \frac{d^2 y'}{dx^2} dx,$$

in which the integrated terms always vanish in virtue of the terminal conditions. In the present case, for example,  $y, y', \frac{d^2 y}{dx^2}, \frac{d^2 y'}{dx^2}$  vanish at each extremity. Thus the left-hand member of (B) vanishes, and we derive

$$\int \{ y' Y - y Y' \} dx = 0. \quad (C)$$

Let us now suppose that  $Y$  vanishes at all points of the bar except in the neighbourhood of  $A$ , and also that  $Y'$  vanishes except in the neighbourhood of  $B$ . Then from (C),

$$y'_A \int Y dx = y_B \int Y' dx;$$

or if  $\int Y dx = \int Y' dx$ ,

$$y'_A = y_B, \quad (D)$$

as was to be proved.

A similar method is applicable to all such cases.

I may here add that, corresponding to each of the statical propositions in my former paper, there are others relating to initial motions in which *impulses* and *velocities* take the place of *forces* and *displacements*. Thus, to take an example from electricity, if  $A$  and  $B$  represent two circuits, the sudden generation of a given current in one of them gives rise to an electromotive impulse in the other, which is the same, whether it be  $A$  or  $B$  in which the current is generated. Or, to express what is really the same thing in another way, the ratio of the currents in  $A$  and  $B$  due to an electromotive impulse in  $B$  is the negative of the ratio of the impulses in  $B$  and  $A$  necessary in order to prevent the development of a current in  $B$ . These statements are not affected by the presence of other circuits,  $C, D$ , &c., in which induced currents are at the same time excited.

Terling Place, Witham,  
January 16, 1875.

XXIII. *Studies on Magnetism.* By E. BOUTY, Professor of Physics at the Lycée of Rheims.

[Concluded from p. 98.]

III. ON THE BREAKING OF MAGNETIZED NEEDLES.

IT has long been known that when a magnet is broken the fragments possess magnetic properties; but I do not think that up to the present any one has set himself to determine the laws which govern the formation of breakage-magnets. In the act of fracture of a magnet we shall distinguish the fact of the separation of the parts (with its consequences, such as would be presented in the case of the simple disjunction of the same parts juxtaposed\*, not welded, in the primitive magnet) from the mechanical fact of the breaking. I purpose, in the first place, to ascertain if this mechanical fact modifies in any way the magnetic state of the fragments. The following are the experiments I have made on this subject.

1. *The proper effect of the Rupture.*

A regular magnetized needle is obtained by passing a freshly tempered steel needle through a spiral traversed by a current. If we break this needle in the middle, two cases may present themselves:—

1st. If the needle is tempered hard enough to break between the fingers like glass, the two halves will be magnets possessing the same magnetic moment, as was to be expected by reason of symmetry.

2nd. If the needle is tempered soft, so as to bend several times in opposite directions before breaking, the two halves possess unequal magnetic moments, in an apparently arbitrary manner.

In the first place this difference must be accounted for. For that purpose I take a needle slightly tempered and regular. I grasp it by the middle between two plates of lead so that one of the halves remains immovable during the breaking, while the other, seized with the hand, is submitted to flexions in opposite directions till rupture takes place. It is found that the half which was submitted to the flexions possesses a lower magnetic moment than that of the half which was nipped, and so much the more as the breaking was more difficult.

\* When two pieces of steel are united by two equal plane faces, the parts opposed to each other are in reality separated by a lamina of air, the thickness of which is very great in proportion to the distance of two magnetic molecules. The thing in question here is perfect juxtaposition, such as exists between the different portions of a coherent solid.

If a needle slightly tempered be grasped on both sides of and very near its middle by means of two pincers, so that only a very thin section on each side of the plane of separation takes part in the flexions which precede rupture, the two halves of the needle present very nearly equal magnetic moments. Therefore the difference above found is due to the flexions which precede the fracture of needles that are tempered soft. It has moreover long been known that mechanical actions of this sort, when *subsequent* to magnetization, diminish the magnetic moment of the needles submitted to them.

In needles that break like glass, the mechanical act of breaking concerns only an infinitely thin layer of molecules on each side of the plane of separation; it must be presumed that the effect of such an action is infinitesimal. I have ascertained that, in the case of hard-tempering, the magnetic moment of a fragment depends neither on the number nor the mode of the breakings by which it has been detached from the mother needle—which would be very difficult to account for if any peculiar appreciable influence were exerted by the act of breaking. In a word, in none of my experiments have I found a weakening of the magnetic moment that could be attributed to such an influence. But proofs still more conclusive will present themselves in the course of this Part.

For all the following experiments I employed only needles of hard and nearly invariable temper—obtained by heating a rectilinear steel wire, of greater length than the needle required, in a gas-flame supplied with air from a bellows, and dipping it when bright-red hot in an earthen pan full of water—the ends being then detached, so as to reserve only the middle portion of the wire, the temper of which is very regular. The length of the needles obtained was, at the most, 150 millims.

## 2. *Saturated cylindrical Needles broken perpendicularly to the axis.*

In his 'Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism' (Nottingham, 1828), Green deduced from the hypothesis of coercive force the following formula, which gives the magnetic moment  $y$  of a needle of length  $x$  magnetized to saturation\* :—

$$y = Aa^2 \left( x - \frac{2}{\beta} \frac{e^{\beta \frac{x}{2}} - e^{-\beta \frac{x}{2}}}{e^{\beta \frac{x}{2}} + e^{-\beta \frac{x}{2}}} \right). \quad \dots \quad (1)$$

\* Beer (*Elektrostatik*) has demonstrated that Green's formula applies to a needle placed in a magnetizing spiral, provided that the turns are of large dimensions in proportion to the diameter of the needle. In that case  $A$  is proportional to the magnetizing force  $f$ .

In this formula,  $A$  is a constant depending only on the nature of the steel, and  $\beta$  a quantity of the form  $\frac{\beta}{a}$ ,  $B$  being a second constant. The diameter of the needles is represented by  $a$ .

The formula is conformable to the results of Coulomb's experiments\*. I propose to verify it for the particular case of needles of very slight diameter and little length.

1. *Needles of the same diameter.*—The temper of the needles compared should be identical; the breaking of a saturated, quite regular cylindrical needle furnishes saturated needles in that condition. They are saturated; for the primitive needle possesses in every point of it a higher degree of magnetism than corresponds to the saturation of the fragment which belongs to it after the breaking. The breaking itself has, according to the preceding, no other effect than that which would result from the separation of the parts which were in precise juxtaposition. Finally, the temper is as identical as possible; we shall even see that employing the results eliminates the minute differences of local temper which cannot be entirely avoided.

The mother needle is magnetized to saturation, by at least four Bunsen elements, in a coil of 25 centims. length, very regular, and formed of three superposed layers of wire. In order to make an experiment, the length and magnetic moment of the entire needle are measured; the two ends are then removed by breaking them off at  $3\frac{1}{2}$  or 4 centims. distance from the extremities, preserving the end fragments; the length of the middle fragment and its magnetic moment are measured, and by successive breakings, each accompanied by two measurements, it is reduced to a length of 1 or 2 millims. The experiment is finished by measuring the length and magnetic moment of the two ends, entire and reduced to successively shorter lengths.

It is rare that all the measurements can be accomplished with one and the same apparatus; two are therefore employed:—one less delicate, for the greater lengths; the other more delicate, for the shorter ones. The ratio of the two apparatus is determined with the greatest care by a number of measurements taken from both.

In order to be clear of all accidental irregularities, the results of the experiments are represented by a curve—the lengths  $x$  of the needles being taken for the abscissæ, and the corresponding magnetic moments for the ordinates. This curve is traced with extreme care by means of the measurements made on the middle fragments of the mother needle. If this needle is saturated, the

\* Coulomb, "Détermination des forces qui ramènent différentes aiguilles aimantées à leur méridien magnétique," *Mém. de l'Institut*, vol. iii.



points characteristic of the end fragments and of the entire needle will fall of themselves on the curve. If this condition is not satisfied, the experiment will be rejected.

Experiment shows that different fragments of the same needle broken before magnetization, magnetized separately to saturation, give points that place themselves on the curve traced from the breaking of one of them (the longest, for instance). This important experiment proves that in the present case the breaking has really no effect at all.

Equation (1) represents a curve tangent to the axis of  $x$  at the origin, and an asymptote to the right line

$$y = Aa^2 \left( x - \frac{2}{\beta} \right). \quad (2)$$

The curves representing the experiments present the same general characters. To make the comparison, the asymptote of the experimental curve is determined with the utmost care. In fact, starting from a length of from 10 to 40 centims. according to the diameter, the points characteristic of the needles fall rigorously in a right line, or only deviate within the limits of errors of experiment; the asymptote is therefore perfectly determined. Let  $D$  be its abscissa at the origin,  $C$  its angular coefficient; the equation can be put in the form

$$y = C \left( x - D \frac{e^{\frac{1}{D}x} - e^{-\frac{1}{D}x}}{e^{\frac{1}{D}x} + e^{-\frac{1}{D}x}} \right). \quad (1')$$

This formula has served for calculating the magnetic moment of short needles; the real moment is determined directly upon the experimental curve.

It is in this way that the following Tables have been formed. The first column contains the lengths of the needles; the second, the observed magnetic moments in arbitrary units; the third, the moments calculated by the formula (1'); the last two, the absolute and relative differences of the observed from the calculated moment.

The experiments were made on needles of 0.175, 0.282, 0.368, and 0.551 millim. diameter. We will confine ourselves to the results furnished by the last three, because the representative curve of the first is too near a right line, for all lengths above 2 millims., for any certain conclusions to be deduced relative to the part of the curve in the vicinity of the origin.

TABLE I.

$$d=0.551 \text{ millim.}, \quad C=\frac{275.5}{16}, \quad D=5.25.$$

l.	M.		$\delta$ .	$\frac{\delta}{M}$ .
	Observed.	Calculated.		
millim.				
1	0.50	0.206	+0.294	0.588
2	1.88	1.575	+0.305	0.162
3	5.60	5.323	+0.277	0.049
4	12.00	10.817	+1.183	0.098
5	20.00	19.113	+0.887	0.044
6	30.00	29.593	+0.407	0.013
7	42.00	41.864	+0.136	0.003
8	55.50	55.336	+0.224	0.002
9	70.20	70.224	-0.024	0.000
10	85.60	85.627	-0.027	0.000

TABLE II.

$$d=0.368 \text{ millim.}, \quad C=\frac{93.25}{12.40}, \quad D=3.6.$$

l.	M.		$\delta$ .	$\frac{\delta}{M}$ .
	Observed.	Calculated.		
millim.				
1	0.30	0.187	+0.113	0.376
2	1.50	1.378	+0.122	0.081
3	3.85	3.101	+0.749	0.194
4	8.50	8.371	+0.124	0.015
5	14.00	13.698	+0.302	0.022
6	20.00	19.994	+0.286	0.014
8	33.85	33.717	+0.133	0.004
10	48.50	48.336	+0.114	0.002

TABLE III.

$$d=0.282 \text{ millim.}, \quad C=\frac{85}{20.70}, \quad D=2.45.$$

l.	M.		$\delta$ .	$\frac{\delta}{M}$ .
	Observed.	Calculated.		
millim.				
2	1.6	1.442	+0.157	0.098
4	7.5	2.107	+0.393	0.052
6	15.0	14.726	+0.273	0.018

Beyond 10 millims. for the thickest needle, and 6 millims. for the thinnest, the characteristic points are, theoretically and practically, confused with the asymptote.

The agreement of calculation and experiment is very remarkable for the needles which are not too short in proportion to their diameter. It was for this case only that Green established the formula which we are engaged in verifying. For extremely short needles, in all the experiments the observed are invariably greater than the calculated numbers. The absolute differences are, it is true, very small; but they exceed the limit of errors of observation, and as much more as the diameter of the needles is more considerable. Nevertheless they are not sufficiently great to permit us to seek empirically the form of the correction which would have to be added to the formula to make it perfectly accurate.

2. *Needles of different diameters.*—For needles of different diameters Green's formula admits of other verifications. The angular coefficient  $C$ , of the asymptote, has to be proportional to the square of the diameter of the needles, and the abscissa at the origin,  $D$ , proportional to their diameter.

It is easy to attach a physical meaning to the quantities  $C$  and  $D$ . Let us consider two needles of the same diameter, sufficiently long for their characteristic points to place themselves sensibly on the asymptote. Their magnetic moments  $y$  and  $y'$  are represented by the corresponding ordinates of the asymptote; that is to say, we have

$$\left. \begin{aligned} y &= C(x - D), \\ y' &= C(x' - D). \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \quad (3)$$

On the other hand, we know, from Coulomb, that in long needles the distance of the poles from the extremities is constant, whatever the length may be. Let  $P$  be that distance, and  $\mu$  the quantity of magnetism of each pole (also constant); we have

$$\left. \begin{aligned} y &= \mu(x - 2P), \\ y' &= \mu(x' - 2P). \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \quad (4)$$

The systems (3) and (4) are incompatible, unless we have at the same time  $C = \mu$  and  $D = 2P$ ; so that the semiabscissa at the origin of the asymptote is equal to the distance of the needle's pole from the corresponding extremity, and the angular coefficient of the same right line is equal to the quantity of magnetism of each pole.

Thus, in the case of long cylindrical needles of different diameters, Green's formula expresses the proportionality of the power of the poles to the square of the diameter, and the pro-

portionality of their distance from the ends of the needle to the first power of the diameter.

Comparison of the results furnished by observation on needles of different diameters is attended with great practical difficulties. The multiplicity of comparisons of apparatus required by these experiments, the considerable influence of the slightest errors in the estimation of the minute diameters upon the ratios to be determined, and, above all, the difficulty of giving an identical temper to needles of different diameters are grave obstacles which it is not easy entirely to surmount. It is right, however, to remark that the difficulty in regard to the tempering is less for needles that are tempered very hard, such as we have always employed, because in this case the coercive power varies little for rather large variations in the temperature at which the steeping was effected.

The following Table relates to the law of the polar distances. The first column gives the diameters of the needles, the second the abscissa  $D$ , the third the value of the ratio  $\frac{D}{d}$  (which should be constant); and the last column gives the differences of the numbers in the third column from their mean.

TABLE IV.

$d$ .	$D$ .	$\frac{D}{d}$ .	$\delta$ .
millim.	millim.		
0·175	1·77	10·113	+0·718
0·282	2·45	8·688	-0·707
0·368	3·60	9·783	+0·388
0·551	5·25	9·528	+0·133
1·036	9·90	9·556	+0·161
1·290	12·40	9·612	+0·307
1·988	16·80	8·451	-0·944

These numbers verify the law, if we take into consideration the above-mentioned multiplicity of the causes of error.

The law relating to the power of the poles is equally well verified, as will be seen in Table V., the third and fourth columns of which give the absolute and relative values of the difference between  $\frac{C}{d^2}$  and the corresponding mean.

TABLE V.—Power of the Poles.

$d$ .	$\frac{C}{d^2}$ .	$\delta$ .	$r$ .
millim.			
0.175	58.719	+3.094	0.055
0.282	51.558	—4.067	0.073
0.368	55.531	—0.094	0.002
0.551	56.695	+1.070	0.019

In short, experiment confirms in a very remarkable manner the various laws contained in Green's formula, except in the case of excessively short needles. It follows that, with the exception mentioned, the distribution of free magnetism in the needles is also represented by the formula given for it by Green, of which our formula is a consequence\*. The quantity of free magnetism in a section perpendicular to the axis, of thickness  $dx$ , situated at a distance  $x$  from the middle, is, according to that formula,

$$Aa^2\beta \frac{e^{\beta x} - e^{-\beta x}}{e^{\beta \lambda} + e^{-\beta \lambda}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$\lambda$  being half the length of the needle. This formula is equivalent to Biot's, and faithfully represents the results of Coulomb's experiments.

*Poles of short needles.*—The magnetic moment of a needle can always be considered as the product of two factors, one of which represents the distance of the poles, the other the quantity of magnetism of each of them. According to Green's formula, the distance of the poles is

$$D = \frac{2\lambda - \frac{2}{\beta} \frac{e^{\beta \lambda} - e^{-\beta \lambda}}{e^{\beta \lambda} + e^{-\beta \lambda}}}{1 - \frac{2}{e^{\beta \lambda} + e^{-\beta \lambda}}}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and the other factor

$$P = Aa^2 \left( 1 - \frac{2}{e^{\beta \lambda} + e^{-\beta \lambda}} \right). \quad . \quad . \quad . \quad . \quad (7)$$

\* The pole is defined as the projection of the centre of gravity of the curve of distribution

$$r = Aa^2\beta \frac{e^{\beta x} - e^{-\beta x}}{e^{\beta \lambda} + e^{-\beta \lambda}}$$

on the magnetic axis of the needle. The distance  $D$  of the two poles has been calculated according to this definition.

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These factors reduce to  $2\lambda - \frac{2}{\beta}$  and  $Aa^2$  respectively for very high values of  $\lambda$ .

On the other hand, the ordinate  $y$  of a curve may always be regarded as the product of the angular coefficient of the tangent at the point considered, into the difference of the abscissa  $2\lambda$  and the abscissa at the origin of the tangent. From these principles the magnetic moment of the needle considered is represented by the product of the two factors

$$\left. \begin{aligned} & 2\lambda - \frac{2}{\beta} \frac{e^{\beta\lambda} - e^{-\beta\lambda}}{e^{\beta\lambda} + e^{-\beta\lambda}}, \\ & 1 - \left( \frac{2}{e^{\beta\lambda} + e^{-\beta\lambda}} \right)^2, \\ & Aa^2 \left[ 1 - \left( \frac{2}{e^{\beta\lambda} + e^{-\beta\lambda}} \right)^2 \right]. \end{aligned} \right\} \dots \dots (8)$$

These factors, like the preceding, reduce to  $2\lambda - \frac{2}{\beta}$  and  $Aa^2$  for very high values of  $\lambda$ . Hence it is that we have before employed the asymptote for determining the polar distance of long needles; but this cannot be extended to the tangents, as I at first expected, since the expressions (8) differ from expressions (6) and (7) by the variable factor  $1 + \frac{2}{e^{\beta\lambda} + e^{-\beta\lambda}}$ . The method which has served us for the determination of the magnetic moments cannot, therefore, enlighten us on the independent variation of the two factors on which they depend.

### 3. *Breaking of non-saturated Needles perpendicular to the axis.*

A. *Regular needles.*—When a needle is magnetized regularly without being saturated, a sufficient length of its extremities can be removed, and then the middle portion can be treated like that thus taken from a saturated needle.

A characteristic curve is obtained tangent to the axis of  $x$  at the origin, and presenting an asymptote the curve of which converges rapidly. The semiabscissa at the origin of this asymptote is the distance of the poles of long rupture-needles (obtained by breaking) from their extremities\*. This distance is therefore constant in rupture-needles as in saturated needles. Moreover two cases are to be distinguished:—

I. When the needles are thin (0.175 to 0.551 millim. diameter) the distance of the poles from the extremities of rupture-needles depends only on the diameter, and is the same as in satu-

\* Demonstration the same as for saturated needles.

rated needles. Indeed the asymptotes of all the curves corresponding to needles of the same diameter cut the axis of  $x$  in exactly the same point. This has been verified

On 3 curves for needles of 0.551 millim.

„ 2	„	„	0.398	„
„ 3	„	„	0.282	„
„ 2	„	„	0.175	„

Further, in the case we are considering, the complete curve is only a proportional reduction of the curve for saturated needles. It is exactly represented, within the same limits, by the equation

$$y = m A a^2 \left( x - \frac{2}{\beta} \frac{e^{\frac{\beta x}{2}} - e^{-\frac{\beta x}{2}}}{e^{\frac{\beta x}{2}} + e^{-\frac{\beta x}{2}}} \right), \quad . . . . (9)$$

in which  $m$  is a factor whose value is less than 1, depending on the degree of magnetization of the mother needle.

TABLE VI.

L.	Curve S.	Curve R.		Difference.
		Observed.	Calculated.	
millim.				
3	5.60	4.40	4.013	+0.387
4	12.00	8.60	8.597	+0.003
5	20.00	14.15	14.317	-0.167
6	30.00	21.00	21.492	-0.492
7	42.00	29.50	30.088	-0.588
8	55.50	39.60	39.760	-0.160
9	70.20	50.50	50.290	+0.210
10	85.60	61.20	61.323	-0.123

The above Table refers to a needle of 0.551 millim. diameter. The second column contains the moment of saturation of the needles as furnished by the experimental curve, and the third the moment of the rupture-needles; the numbers in the fourth column were obtained by multiplying those in the second by the ratio  $m$  of the angular coefficients of the two asymptotes; the fifth column gives the differences between the observed and the calculated numbers.

Above 10 millims. the curves approach very closely their asymptotes, and the comparison which forms the object of this Table ceases to be of interest.

Note that the poles of short rupture-needles are situated the same as if the needles were saturated.

II. These different results do not apply to thicker needles (of 1 to 2 millims. diameter for example). In the first place, the asymptotes to the different curves corresponding to needles of

the same diameter do not meet the axis of  $x$  at exactly the same point, but in points nearer to the origin in proportion as the degree of magnetization of the mother needle is less. Besides, the curves themselves are not proportional reductions of the same curve; and if we take the ratio of the magnetic moment of a rupture-needle to the corresponding saturated needle, this ratio approaches towards unity in proportion as the length of the needle diminishes. Therefore, *if needles be taken from the middle of a non-saturated needle, but which is regular and from 1 to 2 millims. in diameter, the shorter they are the nearer are they to saturation.*

The difference which we have noticed in this respect between very thin and thicker needles is important for the theory of magnetism.

It remains to examine the condition of the end fragments of non-saturated needles. I have limited myself to comparing the magnetic moment of these fragments with that of equal fragments from the middle of the needle. I ascertained that the moment of the end fragments is below that of the middle ones, and as much more so

- (1) As the primitive needle is shorter,
- (2) As the magnetization is less intense,
- (3) As the absolute length of the fragments is less.

The following are some examples :—

I.		millim.
Mother needle	{ Length . . . .	131
	{ Diameter . . . .	2
	{ Moment . . . .	127.3
Divided first into three, then into six equal fragments.		
Ratio of the end third parts to the middle ones		0.803
„ „	sixth parts „ „	0.646

II.		millim.
Mother needle	{ Length . . . .	141
	{ Diameter . . . .	2
Divided into five, then into ten and into twenty equal fragments.		
Ratio of the end fifths to the middle ones		0.751
„ „	tenths „ „	0.544
„ „	twentieths „ „	0.321

In the same experiment, the ratio of the twentieths occupying the second place from the ends, to the middle twentieths, was found to be 0.785.



## III.

*Needles of 2 millims. diameter.*

Needle A.		Needle B.	
	millim.		millim.
Length.....	141	Length.....	143
Magnetic moment.	165.4	Magnetic moment.	46.15
Ratio of the end fourths to the middle ones .....	0.789	Ratio of the end fourths to the middle ones .....	0.709

## IV.

*Needles of 2 millims. diameter.*

Needle A.		Needle B.	
	millim.		millim.
Length.....	122	Length.....	120
Magnetic moment.	135.75	Magnetic moment	50
Ratio of the end fourths to the middle ones .....	0.687	less than .... }	
		Ratio of the end fourths to the middle ones .....	0.662

*B. Needles presenting consequent points.*—We have just seen that, in a regular needle, the fragments from the extremities possess a lower magnetic moment than those which come from the centre.

The consequent points behave like poles of less force than the extreme poles; the fragments which include them possess, with equal length, a higher magnetic moment than that of the end fragments, but lower than that of the fragments derived from the interval between two consequent points.

We conclude this section by indicating a means of verifying the perfect regularity of a magnetized needle:—After separating a sufficient length of the extremities, we break the middle piece into fragments of arbitrary, unequal lengths. If the mother needle was regular, the characteristic points obtained by taking for abscissa the length of the fragments, and for ordinate their magnetic moment, will be situated on a regular curve. The slightest irregularities will then be seen by simple inspection of the figure obtained.

4. *Separation, parallel to the axis, of Prismatic Bundles.*—  
*Observations on the Temporary Magnetism of Steel.*

The difficulty of breaking a needle along a plane parallel to its axis induced us to investigate the more practical case of superposed strips composing a bundle. The results furnished by this examination apply only approximately to breaking, since the latter may be regarded as the extreme case of separation—when the parts facing each other on both sides of the plane of separation are at an indefinitely minute distance.

We form a prismatic bundle with a number of pieces of watch-

spring. The bundle, tempered and magnetized all in one piece, is afterwards divided.

If the mother needle (the bundle) is saturated, we find that the separate laminæ are not. This is not surprising; for the superposed laminæ react on one another in a direction the reverse of their magnetization, and consequently the permanent magnetic moment which they can attain while united is less than if they were separate; but what does at first appear astonishing is that the sum of the magnetic moments of the separate laminæ is considerably greater than that of the primitive bundle.

This last fact is well brought out by making the experiment in the following manner. I take a bundle which is square in section, formed by the union of four square bars of the same length. This combination is tempered hard and immediately magnetized; I measure its magnetic moment, and then take it to pieces and measure the moment of each bar separately. The sum of the moments is found to amount to very considerably more than the magnetic moment of the united bars. Joining the bars together in twos, the sum of the moments of these partial bundles is intermediate to those of the total bundle and of the separate bars. And, finally, if we reconstitute the primitive bundle, the magnetic moment returns to its first value.

In this experiment the bundle, which, innocent of any previous magnetization, has only once undergone the action of the magnetizing spiral, is in an absolutely normal condition at the instant of the first separation; and we do not see that any new magnetic force interposes to which we might attribute the observed augmentation of permanent magnetism. It is true that by separating the bars we suppress their mutual reaction, and we know that in each of them it acts in opposition to the permanent magnetism; but that can have no other effect than to cause a certain amount of temporary magnetism to disappear. Thus, in a *normal* bar, a certain quantity of permanent magnetism is superposed to a temporary magnetism opposite in direction, which latter the removal of a magnetic layer parallel to the axis causes to vanish.

This curious superposition may be observed in other circumstances. It is known, for instance, that if a magnetized bar of steel be submitted to the action of a current of too little intensity to demagnetize it entirely, during the action of the current there is observed a diminution of the bar's magnetism, which may proceed even to the reversal of the poles, while it is found after the cessation of the current that the bar is magnetized in the primitive direction. It is also known that, if the south pole of a powerful bar magnet be presented to the south pole of a magnetized needle, the repulsion which is manifested at a great

distance may be transformed into attraction at a very short distance, in consequence of the temporary magnetism developed by induction. This fact was observed in the last century by Muschenbroek and Epinus.

The phenomena connected with temporary magnetization play a great part in all questions relative to the breaking of magnets. Let us consider generally two bodies, A and B, submitted to the action of one and the same inductive force, but constantly united to one another. After the cessation of the inductive force the body A remains under the action of B, and retains, apart from the residual magnetic moment which it would retain after the removal of B, a moment produced by influence, which is compounded with the former, and which is permanent only so long as the union of A and B subsists. It might be named the *subpermanent* moment. The same reasoning applies if A and B are two portions of one and the same body; and it is evident that to determine the permanent moment taken by a body under the action of an inductive force is an eminently complex problem, and one that can only be solved generally by knowing the laws of temporary as well as permanent magnetism properly so called. We commend this consequence to the attention of investigators of the theory of magnetism.

In the experiment of the bundle broken parallel to the axis the subpermanent is opposite in direction to the permanent magnetism. On the contrary, the two are identical in direction in the case of a needle broken in a plane perpendicular to its axis, and of which the fragments are separated or reunited end to end. The moment of the fragments brought into contact is greater than the sum of the moments of the separated fragments, and yet falls short of the value of the moment of the entire needle before it was broken. This is readily verified by experiment.

#### IV. ON THE THEORY OF STEEL MAGNETS.

The physical theory of magnetism exists almost entirely under the form of comparisons. As in nature there cannot be two series of phenomena absolutely parallel, unfortunately those comparisons only awaken in the mind ideas which are imperfect and never entirely satisfy it. Even Ampère's beautiful theory of molecular solenoids is, perhaps, not wholly unaffected by this remark, which applies especially to the coercive-force theory, as well as to all other attempts which have been made for the purpose of elucidating the theory of steel magnets.

It was Coulomb who first established with some precision the difference between iron and steel in regard to magnetization, and introduced the notion of *coercive force*. He compares the

effect of this force to a sort of friction which opposes the separation of the combined magnetic fluids, or their reunion when they are separated. This comparison between two orders of phenomena so complex and so little understood as magnetization and friction is necessarily very artificial, and excludes a great number of phenomena furnished by experiment. In fact, the assumption of a coercive force analogous to friction would seem to imply the following propositions:—

1. The coercive force is opposed to any induction-effect on the part of magnetic forces below a certain limit  $C$ .

2. It reduces the effect of any force  $F > C$  to that which would be produced by a force equal to  $F - C$ , if the coercive force did not exist; and

3. After the cessation of  $F$  it preserves the acquired magnetism up to a limit equal to the magnetism which would be produced by a force  $C$  continuing to act in the direction of the force  $F$ , if the coercive force had no existence.

The only mathematician who, to my knowledge, has treated a problem in the hypothesis of the coercive force, Green, does not appear to have formed a different idea of it.

In order to appreciate the experimental value of the hypothesis, we have only to compare the three preceding propositions with three others which we will borrow from a paper by Mr. Rowland\*, and which, founded on experiment, agree also perfectly with all the known facts.

“1. *Nearly or quite all the magnetism of a bar is, with weak magnetizing forces, temporary; and this is more apparent in steel than in soft iron.*

“2. *The temporary magnetism increases continually with the current.*

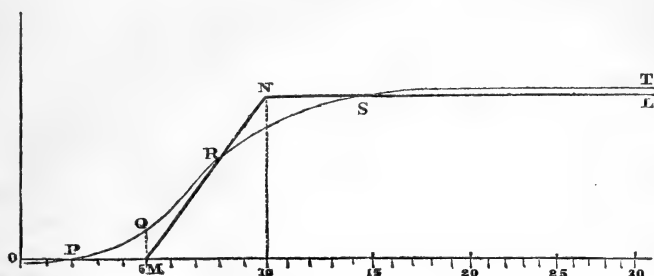
“3. *The permanent magnetism at first increases very fast with the current, but afterwards diminishes as the current increases, when the iron is near its maximum of magnetism.*”

It is remarkable that, if the hypothesis of the coercive force is incapable of representing the whole of the phenomena, it nevertheless represents very well the course of the permanent magnetization. We reproduce (fig. 6) a curve drawn by Rowland after his experiments, taking for abscissæ the magnetic forces, and for ordinates the corresponding magnetic moments acquired permanently by the unit of volume of a cylinder of indefinite length: it is the curve  $OPQRST$ . We insert also a broken line  $OMNL$ , which reproduces in general features the course of the curve: this corresponds to the hypothesis of the coercive force by making  $C=5$  and supposing that the perma-

\* Phil. Mag. August 1873.

nent magnetism produced by a force  $F$  comprised between  $C$  and  $2C$  is proportional to  $F - C$ .

Fig. 6.



The original hypothesis of the coercive force explains, therefore, pretty accurately the only phenomena well known at the time when it was invented; it cannot enable us to foresee new phenomena; and the progress of the science of magnetism has left little of it in existence but the name.

The phenomena of temporary magnetism and of the maximum of magnetization, as well as those of permanent magnetism, have been explained collectively by Wiedemann, but again by means of a comparison. He compares magnetic phenomena to those which depend on the elasticity of solid bodies, specially those accompanying torsion or flexion. This has the advantage of expressing an incontestable physical relation, since torsion modifies the magnetic condition of a bar, and such modifications may in their turn cause a variation in the torsion to which the bar has been submitted beforehand.

Wiedemann assumes that in the unit of volume of iron or steel a finite number of magnetic elements (molecular currents) exist, but that in the natural state their axes are distributed equally in all directions. External magnetic forces tend to rotate these elements about their centre of gravity; but these oppose a resistance to displacement, analogous to elastic reaction, in such a manner that, according to the intensity of the acting forces, the elements retain permanently a more or less considerable portion of their temporary displacement. On submitting these hypotheses to calculation we obtain, for the representation of the temporary and the permanent magnetisms, curves which, though satisfying the same essential conditions, present only vague and general relations with the curves furnished by experiment.

For the very ingenious developments given by this author to his theory the original work must be consulted\*. We will

\* *Galvanismus*, vol. ii.

merely say that the analogy on which it rests may be carried very far, and that we could find arguments in favour of it even in our present researches : thus we have seen that repetition of the action of a current upon a needle augments the permanent magnetic moment communicated to the latter \* ; in like manner, when an imperfectly elastic thread is twisted by means of a constant force, the permanent torsion it acquires is increased by a second or a third application of the same force, and tends towards a new limit.

We do not charge Wiedemann's hypothesis with being absolutely false ; we only say that it is incomplete ; and this is why a certain number of phenomena can only with extreme difficulty be accommodated to it. Of this number are some relative to the superposition of a certain permanent magnetism and a temporary magnetism opposite in direction, particularly those produced in the separation of magnetized bundles †.

Instead of attributing, as Wiedemann does, temporary and permanent magnetism to the same molecules, other physicists ‡ prefer to assume that the condition (whatever it may be) which corresponds to the conservation of a certain degree of permanent magnetism is communicated, in the steeling or the tempering, only to a certain number of molecules, the rest retaining the magnetic properties of soft iron. It is further conceivable that the different molecules may acquire the coercive power in different degrees.

Be this as it may, I think that important light would be shed on many facts in connexion with the magnetization of steel by supposing that it is magnetically heterogeneous. Now this is not a gratuitous hypothesis. Chemists will readily admit that the true nature of the chemical species which constitute steel is still very imperfectly known, and that a bar of steel may contain normally a mixture of several of those species. When a steel bar is attacked by chlorhydric acid, it is ascertained, according to A. Holtz §, that the corroded surface is rugous, the asperities being formed of a highly carbonaceous steely substance (*Kohleneisen*) scarcely or not at all capable of being attacked by the acid ; and the arrangement of this substance in the interior

\* *Vide supra*, Part II. sect. 2 (pp. 90-98).

† When an imperfectly elastic thread has undergone a permanent torsion, a temporary torsion in the opposite direction can, it is true, be superposed to the permanent one by the application of a force insufficient to untwist it entirely. But how can a temporary torsion be associated with a permanent one in the opposite direction in a thread submitted only once to torsion and then left to itself? But this is what happens in magnetization (see above, p. 197 et seq.).

‡ See Verdet, *Conférences de Physique faites à l'Ecole normale*, p. 219.

§ Pogg. *Ann.* vol. cli. 1874.

is variable in different bars : sometimes it forms a sort of network with closed meshes, filled up with the more attackable ferruginous mass ; sometimes the two substances are more intimately mixed, and the carbonaceous steel is in fine isolated grains. Physical heterogeneity involves magnetic heterogeneity ; Holtz, in fact, having measured the magnetic moment of magnetized bars before and after the more or less prolonged action of chlorhydric acid, believes it to be deducible from the whole of his experiments that the carbonaceous steel is the *real seat of the coercive force*, and that the rest of the mass is almost destitute of it.

It is not for us to pass judgment on the degree of confidence deserved by A. Holtz's conclusions from the chemical point of view ; but the hypothesis of the magnetic heterogeneity of steel does appear to merit serious examination. In the first place, it has the advantage of affording a very simple explanation of the phenomena connected with the superposition of temporary and permanent magnetism, for which it was imagined. If, moreover, we consider (1) that the laws of the temporary magnetism of steel differ in nothing essential from those of induced magnetism in soft iron, and (2) that the development of permanent magnetism is eminently variable from one species of iron or steel to another, and for one and the same species, according to physical conditions sometimes insignificant, we shall be induced to attribute to this hypothesis a certain degree of probability.

In any case the study of mixed magnets would be truly interesting, apart from the hypothesis which led us to undertake it. On this we shall only say a few words here, reserving to ourselves to return to a subject which can be fully elucidated only by long series of experiments.

*Theory of a Mixed Magnet.*—Let us imagine a cylinder of elementary dimensions, but of very great length compared with its diameter. Suppose it to be formed by the combination of two sorts of magnetic elements, scattered at random, but in a determinate proportion in every part of the cylinder. The elements A, endowed with coercive power, are such that they conserve all the magnetism which they acquire ; while the elements B are absolutely destitute of coercive power.\*

Let a magnetic force  $F$  act in the direction of the axis of the cylinder, and let  $kF\Delta v$  be the magnetic moment which the cylinder would receive if the molecules B existed alone.  $\Delta v$  represents the volume of the cylinder, and  $k$  a coefficient which depends on the density\* of the elements in question. In like

\* That is to say, on the number of elements contained in the unit of volume.

manner, let  $qF\Delta v$  be the moment corresponding to the elements A, supposing them to be alone. Every molecule of the system B is acted on, not only by the external force, but also by the system A, and *vice versa*. This reciprocal action, in the same direction as the external force, has the effect of raising the total magnetism above the sum  $(k+q)F\Delta v$ .

If, in order to simplify, we suppose the coefficients  $k$  and  $q$  independent of  $F$ , which will be sensibly true for small values of the inductive forces, the final moment of each of the two systems will be found by a very simple reasoning copied from the elementary theory of electrical condensation\*. Designating then by  $c$  and  $d$  two coefficients depending on the mean grouping, and also on the density of the elements of the two systems, we find, for the final moment  $M_a$  of system A,

$$M_a = qF \frac{1+ck}{1-cdkq} \Delta v; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and in the same way,

$$M_b = kF \frac{1+dq}{1-cdkq} \Delta v; \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence the total moment

$$M = M_a + M_b = F \frac{q+k+(c+d)kq}{1-cdkq} \Delta v. \quad . \quad . \quad . \quad (3)$$

If the action of the force  $F$  be suppressed, the molecules A conserve their magnetism. As to the molecules B, they are now under the action of the system A only, which is equal to  $dqF \frac{1+ck}{1-cdkq}$ ; they retain a moment

$$M'_b = gkdF \frac{1+ck}{1-cdkq} \Delta v. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The total residual magnetism is

$$m = M_a + M'_b = qF \frac{(1+ck)(1+dk)}{(1-cdkq)} \Delta v; \quad . \quad . \quad . \quad (5)$$

and the magnetism called *temporary*, which disappears through the cessation of the current, is

$$\mu = M - m = kF\Delta v. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The coefficient  $k$  is what is usually called the *coefficient of tem-*

\* We know very well that this theory is not rigorously exact; but what is required here is merely to get a general idea of the phenomena. Besides, we are supported by the example of M. Jamin, who introduced into science the expression "magnetic condensation," in his theory of the effect of contacts of soft iron.



porary magnetism ; and the quantity which plays the same part in the expression of  $m$ ,

$$q \frac{(1 + ck)(1 + dk)}{1 - cdkq},$$

is called the *coefficient of permanent magnetism*.

The quantity really comparable to the coefficient  $A$  is, from the foregoing, the coefficient  $q^*$ .

It is evident, and without difficulty verified in a particular case, that the total magnetic moment  $M$  lies between those which would be produced by the same force  $F$  acting on two cylinders equal to the first, each of which comprised only one species of molecules, with the same total density. But the same is not true of the residual moment  $m$ , which for a given value of  $q$  is greater in proportion as the coefficient of temporary magnetism of the soft iron is itself greater ; and as this last coefficient is enormous, it is evident that the addition of a certain quantity of soft iron to the hardest steel can augment the residual moment of the latter.

It will be recollected that, according to M. Jamin, the varieties of steel which are the richest in carbon and of the hardest temper do not exhibit the most powerful residual moments ; and it should be so if the molecules of soft iron in them are very rare, as we must suppose them to be.

#### RECAPITULATION.

We have indicated a new method for comparing the magnetic moments of very small magnetized needles.

We have investigated the effect produced upon a magnet by repeatedly passing it to the spiral, by interruption or reestablishment of the inducing current, &c., and have given empiric formulæ fitted to represent the results obtained.

We have studied the effects of the breaking and division of cylindrical and prismatic magnets, either perpendicularly or parallel to the axis, and verified by experiment, in the case of needles of small diameter, an important formula given by Green to represent the magnetic moment of saturated needles of various lengths and different diameters.

Lastly, on the ground of the peculiar facts examined in this memoir, as well as the whole of the known facts, we have shown

\* If the coefficients  $c$  and  $d$  be supposed equal, the formulæ will be a little simplified (see *Comptes Rendus de l'Acad. des Sciences*, Feb. 23, 1874). Only a complete theory could explicitly state the values of the four coefficients  $k$ ,  $q$ ,  $c$ , and  $d$  as functions of the densities  $\delta$  and  $\delta_1$  of the two kinds of elements, and consequently establish relations between these four quantities.

the insufficiency of present theories of magnetism to explain the various peculiarities of the temporary magnetism of steel; and we have suggested that, in regard to the magnetic properties of its elements, that substance must be considered a heterogeneous mass.

#### XXIV. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE\*.

##### II.

##### *Cryogens and Cryohydrates.*

BY Cryogen I mean an appliance for obtaining a temperature below  $0^{\circ}$  C. In this paper it always signifies a freezing-mixture. By Cryohydrate I mean the body resulting from the union of water with another body, and which hydrate can only exist in the solid form below  $0^{\circ}$  C. As this communication is in every respect continuous with the one brought before the Physical Society on November 7th, 1874, and published in the Philosophical Magazine for January 1875, the paragraphs are numbered in sequence with those of the previous communication.

##### CRYOGENS.

##### *Precision of Temperature of Freezing-mixtures.*

§ 41. In § 39, when I was speaking of the possible uses of cryohydrates for the maintenance of constant temperatures, I said:—"With the exception of the melting-points of a few organic bodies such as benzol, and the boiling-points of a few liquids such as liquid ammonia, sulphurous acid, and carbonic acid, and the rather ill-defined temperatures to be got by various freezing-mixtures, there are no means in the hands of physicists for obtaining and maintaining with certainty and ease a fixed temperature below  $0^{\circ}$  C."

In regard to freezing-mixtures, I confess to have been here very much misled by the confident but rather erroneous statements of others, to which I attached faith trebly blind—blind, because no recorded experiments really support them, blinder still because a little thought in the right direction must have shown their fallacy, and blindest of all because the one experiment of my own in this direction (§§ 16 and 17) shows that the minimum temperature of an ice-salt cryogen is reached whether we take the ratios 3 of salt to 1 of ice or 1 of salt to 2 of ice, and so points to the wideness of the margin of ratio which may obtain between the weights of ice and the salt. It will further be shown in

\* Communicated to the Physical Society, Jan. 18th, 1875.

§§ 44-46 that the temperature of the constituents has nothing to do with the temperature reached, and in § 49 that the degree of hydration of the salt employed is often without effect.

Accordingly I unqualifiedly withdraw the expression "ill-defined" as applied to freezing-mixtures. They may be, on the contrary, bodies of precise temperature under widely varying circumstances.

§ 42. The enormous latent heat of water, the fact that the specific heat of ice is only about half that of water, while the specific heats of all salts are far less than that of ice, and therefore, *à fortiori*, less than that of water, together with the good thermal conductivity of water, all argue that, if constantly stirred, all parts of a freezing-mixture will have the same temperature. The fact that the liquid portion of a freezing-mixture of ice and a solid salt is the cryohydrate of that salt, ensures the identity of the resulting temperature under various conditions of proportion. The constant tendency to the formation of this cryohydrate by contact between the solids is always seeking to depress the temperature; while the solidification of the cryohydrate at an indefinitely small fraction of a degree below the temperature of the freezing-mixture, and the consequent liberation of heat, ensures the temperature against such fall.

Statements therefore, whether previously made by myself or others, that it is advantageous to weigh the salt and ice in definite proportion, that the ice should be dry, that snow is preferable to ice on account of its state of finer division, that additional cold is produced by previously cooling the ice or salt or both, are to be put aside as untrue—untrue, that is, as far as the temperature or heat-tension is concerned. To obtain the greatest quantity of heat-absorption with a given amount of salt, such a quantity of ice must be taken as will form with the salt a cryohydrate. The proportions can be at once gathered from Table X. § 90.

§ 43. Further, the fact that all cryohydrates, with, I believe at present, the sole exception of sulphate of zinc and chloride of magnesium, have far more water than that ordinary hydrate which has most water, shows that it cannot matter whether a salt which affects water of crystallization be employed in the anhydrous state or with its crystalline water.

It may, however, be otherwise with salts containing the elements of water more intimately associated; and, as we shall see in one case at least, an anhydrous compound may melt ice with which it is in contact and heat the so-formed water far above zero, while the compound so formed, when cool, will when mixed with a fresh quantity of ice absorb heat abundantly. I suppose in such cases double decomposition ensues; and though nothing

is eliminated, there is a rearrangement of the elements more intestinal than that effected by the association with water.

§ 44. *Effect of the Temperature of the Ingredients on that of the Freezing-mixture.*—An ounce of finely powdered chloride of sodium was cooled in a flask surrounded by a freezing-mixture till its temperature was  $-15^{\circ}$  C. It was then stirred with four ounces of ice, which had been cooled and had the temperature  $-10^{\circ}$ . As soon as liquefaction began, the temperature  $-22^{\circ}$  was reached; and this degree of cold was never surpassed.

§ 45. The same degree of cold ( $-22^{\circ}$ ) resulted from the mixture of 1 oz. of NaCl at  $-15^{\circ}$  with 4 oz. of ice at  $0^{\circ}$ , also when 1 oz. of salt at  $+12^{\circ}$  C. was mixed with 4 oz. of ice at  $-12^{\circ}$  C.

§ 46. Indeed the margin of temperature may be greatly extended. Thus, 1 oz. of NaCl in powder was heated to incipient redness and thrown upon 5 or 6 oz. of ice at  $0^{\circ}$ ; after a few minutes constant stirring, the temperature had reached  $-22^{\circ}$ .

§ 47. 1 oz. of dry anhydrous  $\text{Na}_2\text{SO}_4$  was heated nearly to redness, and thrown upon 4 oz. of ice at  $0^{\circ}$ . In a few minutes the temperature had sunk to  $-0^{\circ}7$ . Again, an ounce of anhydrous  $\text{CuSO}_4$  was heated to about  $600^{\circ}$  C., and thrown upon 4 oz. of ice; the temperature at once sank to  $-0^{\circ}5$  (compare § 55).

§ 48. From the above experiments, and from the theoretical considerations touched upon in § 42, I conclude that, within very wide limits as to quantity, the temperature of a freezing-mixture may be very independent of the temperature both of the salt and of the ice.

§ 49. *Effect of Crystalline Water in the salt on the Temperature of the Freezing-mixture.*—From § 26 it appears that crystallized sulphate of soda ( $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$ ) gives with ice a temperature of  $-0^{\circ}7$ . Deprived of water, the anhydrous salt  $\text{Na}_2\text{SO}_4$  gave with ice the temperature also of  $-0^{\circ}7$ . Sulphate of copper in the anhydrous state produced, when mixed with ice, a temperature of  $-1^{\circ}7$ , while with the ordinary crystallized hydrate the temperature was  $-2^{\circ}$ .

§ 50. Having examined six or seven other salts as to the temperature of their freezing-mixtures when employed both with and without their crystalline water, I do not scruple to assert that water of crystallization, properly so called, takes no effect upon the temperature of the freezing-mixture; and I believe the same is true of that water which has been called constitutional. But where a profound rearrangement of the elements of water ensues, the effect may be different, as appears in the next paragraph.

§ 51. The chloride of aluminium,  $\text{AlCl}_3$ , as offered in com-

merce, fumes strongly in the moist air, so great is its avidity for water. Thrown upon several times its own weight of ice, the two liquefy and the temperature stands above  $0^{\circ}$ . The strongest commercial solution of chloride of aluminium, however, when at the temperature of the air or at  $0^{\circ}$  or at  $100^{\circ}$  C., will reduce the temperature to  $-13^{\circ}$  when poured upon three or four times its own weight of ice. I suppose the anhydrous chloride may be viewed as separating the atoms of the water-molecule, as is supposed to be the case with the chlorides of phosphorus.

§ 52. *Hydrochloric Acid as a Cryogen with Ice.*—Ordinary commercial hydrochloric acid when poured upon ice may produce as much as  $22^{\circ}$  of cold. The amount of HCl in the hydrochloric acid, however, is here to be as much considered as it would have to be if we dealt with ice and a solution of NaCl. In the experiments which are given in the succeeding paragraphs as far as § 54, the hydrochloric acid employed was formed by saturating water with the gas, while the liquid was kept after absorption had ceased for half an hour at  $0^{\circ}$  while the acid passed through. The barometric pressure was 770 millims. This may be considered a normal acid.

§ 53. The acid at  $0^{\circ}$  was poured in various proportions upon ice at  $0^{\circ}$ . Fifty grms. of ice were used in each experiment. The Table shows within what small limits of ratio the minimum temperature is reached. In the Table the weight of the ice is taken as unity.

Weight of ice at $0^{\circ}$ C.	Weight of HCl + $n\text{H}_2\text{O}$ at $0^{\circ}$ C.	Resulting Temperature.
1	1.5	$-3\frac{2}{3}$
1	0.4	$-26$
1	0.3	$-23$
1	0.2	$-19$

We are therefore, when dealing with a cryogen one of whose constituents is a liquid, much more limited in the range of ratio which we may employ to procure the maximum cold than is the case when both are solid.

§ 54. Accordingly, in examining the effect of the alteration in the temperature of one or both of the constituents, it is necessary always to use the same ratio. In the Table below, the ratio used was that which gave the maximum cold when both were at  $0^{\circ}$  C., namely 1 of ice to 0.4 of the saturated solution of HCl. It must be understood that in those cases where the hydrochloric solution was used below  $0^{\circ}$  C., it is not meant that the saturation with HCl took place at that lower temperature, but that, having been saturated at  $0^{\circ}$ , the solution was subsequently cooled to the lower temperature.

1 ice at $-15^{\circ}$	with 0.4 HCl sol. at $0^{\circ}$	gave $-28^{\circ}$ .
1 " $0^{\circ}$	" 0.4 " "	$-15^{\circ}$ " $-27^{\circ}$ .
1 " $-15^{\circ}$	" 0.4 " "	$-12^{\circ}$ " $-27^{\circ}$ .

All these numbers are sufficiently near to  $-26^{\circ}$ , the number got when both ingredients are at  $0^{\circ}$ , to justify the conclusion that the temperature of the ice has something, but little, to do with the temperature of the freezing-mixture. And it appears that the temperature of the HCl solution is also without effect, provided that the saturation has been effected at the same temperature and pressure. The water acts, indeed, here much as the water of crystallization acts in the case of solid salts.

§ 55. *Table of Freezing-mixtures.*—In the following Table the lowest attainable temperature is given. This, as we have seen, is independent of the temperature of the salt and its degree of crystallization. The temperatures are got on mixing the salt with three to six times its weight of ice in lumps of the size of a pea downwards. The salts are arranged according to the degree of cold they furnished.

TABLE IX.—Freezing-mixtures.

	$^{\circ}$ C.		$^{\circ}$ C.
NaBr . . . . .	$-28.0$	KCl . . . . .	$-10.5$
NH <sub>4</sub> I . . . . .	$27.0$	K <sub>2</sub> CrO <sub>4</sub> . . . . .	$10.2$
	$28.0$	BaCl <sub>2</sub> +2H <sub>2</sub> O . . . . .	$7.2$
NaI . . . . .	$26.5$	Sr <sub>2</sub> NO <sub>3</sub> . . . . .	$6.0$
CuCl <sub>2</sub> . . . . .	$24.5$	MgSO <sub>4</sub> +7H <sub>2</sub> O . . . . .	$5.3$
KI . . . . .	$22.0$	ZnSO <sub>4</sub> +7H <sub>2</sub> O . . . . .	$5.0$
NaCl . . . . .	$22.0$	KNO <sub>3</sub> . . . . .	$3.0$
MgCl <sub>2</sub> +6H <sub>2</sub> O . . . . .	$20.5$	Na <sub>2</sub> CO <sub>3</sub> . . . . .	$2.2$
SrCl <sub>2</sub> +6H <sub>2</sub> O . . . . .	$18.0$	CuSO <sub>4</sub> +5H <sub>2</sub> O . . . . .	$2.0$
2NH <sub>4</sub> SO <sub>4</sub> . . . . .	$17.5$	FeSO <sub>4</sub> +7H <sub>2</sub> O . . . . .	$1.7$
NH <sub>4</sub> Br . . . . .	$17.0$	K <sub>2</sub> SO <sub>4</sub> . . . . .	$1.5$
NH <sub>4</sub> NO <sub>3</sub> . . . . .	$17.0$	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> . . . . .	$1.0$
NaNO <sub>3</sub> . . . . .	$16.0$	Ba <sub>2</sub> NO <sub>3</sub> . . . . .	$0.9$
NH <sub>4</sub> Cl . . . . .	$16.0$	Na <sub>2</sub> SO <sub>4</sub> +10H <sub>2</sub> O . . . . .	$0.7$
FeCl <sub>3</sub> (commercial) . . . . .	$16.0$	KClO <sub>3</sub> . . . . .	$0.7$
Ca <sub>2</sub> NO <sub>3</sub> +4H <sub>2</sub> O . . . . .	$14.0$	AlNH <sub>4</sub> 2SO <sub>4</sub> +12H <sub>2</sub> O . . . . .	$0.4$
KBr . . . . .	$13.0$	HgCl <sub>2</sub> . . . . .	$0.2$
AlCl <sub>3</sub> in strong sol. . . . .	$13.0$	NH <sub>4</sub> CO <sub>2</sub> . . . . .	$0.2$

We shall study this Table in connexion with the temperature and molecular ratios of the cryohydrates of the same salt.

## CRYOHYDRATES.

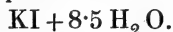
*Cryohydrates of the Halogen Alkalies.*

§ 56. As was anticipated in § 31, the study of the nine salts

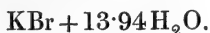
resulting from the union of the halogens with the alkali metals has brought to light many points of interest. The two members of this family which I had previously examined were  $\text{NaCl}$ , solidifying at  $-23^\circ$  with 10.5 molecules of water, and  $\text{NH}_4\text{Cl}$ , solidifying at  $-16^\circ$  with 12 molecules of water. I have reexamined the cryohydrate of chloride of ammonium; and the mean of several analyses gives 19.27 per cent of chloride, which brings the ratio to  $\text{NH}_4\text{Cl} + 12.4 \text{H}_2\text{O}$ .

There is nothing particular to remark in the analysis of this group. All, excepting the ammonium salts, bear heating to  $300^\circ$  or  $400^\circ \text{C}$ . without decomposition or volatilization. The liquid cryohydrates were weighed in covered basins of Bohemian glass, evaporated to dryness, strongly heated, covered, and quickly cooled. The ammonium salts were heated on the water-bath till they ceased to lose weight.

§ 57. *Iodide of Potassium*.—This salt, which at the ordinary temperature is so abundantly soluble in water, yields a large proportion of anhydrous salt when cooled. An ice-salt cryogen fails to solidify it, but just brings it to the verge of solidification, removing all the free salt in the same manner as it does with  $\text{NaCl}$  solution, excepting that there does not appear to be any intermediate cryohydrate corresponding with  $\text{NaCl} + 2\text{H}_2\text{O}$ . The  $\text{KI}$  solution appears to be homogeneous at  $-8^\circ$  or  $-12^\circ$ . When subjected to solid  $\text{CO}_2$  and ether, it at once begins to solidify at  $-22^\circ$  to  $-23^\circ$ , and retains this temperature to dryness. Of the four parts into which the substance was divided as it solidified, two were analyzed—namely, the second crop of crystals, and the finally solidified and remelted mother-liquor. Of the first, 5.8240 grms. gave 3.0120 anhydrous  $\text{KI}$ , or 51.72 per cent.; of the second, 6.3960 grms. gave 3.331, or 52.07 per cent. The latter corresponds to the molecular ratio

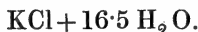


§ 58. *Bromide of Potassium*.—This forms a cryohydrate of great beauty. At  $-13^\circ$  the characteristic crystals are seen to be produced. They have the fern-like shape of ice-crystals. The fronds are studded with a fructification of opaque crystals, whose opacity seems to spread through the at first transparent fronds till the whole resembles frosted silver. The two portions which were taken for analysis were the final part, or that which solidified last, and the immediately preceding crop of crystals. Of the former, 7.8285 grms. gave 2.5170 of  $\text{KBr}$ ; of the latter, 9.4560 grms. gave 3.0070 dry salt. These correspond respectively with 32.15 and 31.80 per cent. The first points to the molecular relationship



§ 59. *Chloride of Potassium*.—Since KI is thus seen to combine with 8·5 of water and KBr with 14 of water, the one a fraction and the other a whole number, I spared no care in the preparation and analysis of the chloride of potassium, to see whether the fractional relationship did not arise from experimental error. Perfectly pure  $K_2CO_3$  was dissolved in a slight excess of HCl, evaporated to dryness, and ignited in a platinum basin. The KCl was recrystallized four times. Six ounces of the saturated solution were cooled; solid matter separated down to  $-10^\circ$ . At this temperature the separated salt appeared as a cloudiness in the liquid, a little heavier than the latter, and of a granular but translucent appearance. The liquid may now be cooled to  $-15^\circ$ ; but it is now a supersaturated solution of the true cryohydrate—a solution, it is to be observed, of which the solid crystals present are unable to determine the solidification. At a little below  $-15^\circ$ , long ice-like crystals shoot out and the temperature rises to  $-11^\circ\cdot4$ , which is the crystallizing-point of the cryohydrate. From this behaviour I am disposed to admit that there may be an intermediate hydrate similar to the bihydrate of NaCl.

Of the last portion which solidified, 6·588 grms. gave 1·320 of anhydrous salt. Of the previous crop of crystals 7·869 grms. gave 1·579 of salt. These show the respective percentages 20·03 and 20·07, both of which point to the relationship



§ 60. The halogen salts of potassium arrange themselves according to the cold required for the solidification of their cryohydrates, and according to the molecular ratio of water, as follows:—

	Solidifying-temperature of cryohydrate.	Number of molecules of water to 1 of salt.
KI . . .	$-23^\circ$	8·5
KBr . . .	$-13^\circ$	14·0
KCl . . .	$-11\cdot4^\circ$	16·5

We find here the general rule confirmed, that among like salts the lower the temperature of solidification of the cryohydrate, the smaller is the number of molecules of water which it contains.

§ 61. *Iodide of Ammonium*.—This salt gave me considerable trouble. It is difficult to obtain in perfectly colourless crystals; and both the solid and its solution are disposed to change colour, becoming brown when kept, even in the dark. Heating in a water-bath with constant stirring restores the dry altered

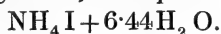


salt to a light-grey colour. Analysis showed that this coloration did not sensibly affect the percentage composition of the salt; but still its power of assuming water might be seriously affected. A saturated solution was exposed for some hours to an ice-salt cryogen at  $-22^{\circ}$ ; it was then exposed to the carbonic-acid-and-ether cyanogen. It solidified wholly at from  $-27^{\circ}$  to  $-28^{\circ}$ . While solidification is taking place, the cryohydrate is nearly perfectly white. When dry and over-cooled, it assumed a pinkish grey colour, resembling chloride of silver which is beginning to be affected by light.

The analysis of these portions is given, namely:—(1) the last to solidify or remelted mother-liquor; (2) the immediately preceding crop of crystals; and (3) the crop before (2). As the results are by no means in good accord, I give them all:—

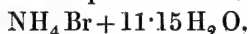
	Solution.	$\text{NH}_4\text{I}$ .	per cent.
(1) . . . .	5.2935	gave 2.9375,	or 55.49
(2) . . . .	5.4960	„ 3.2120,	„ 58.42
(3) . . . .	8.4560	„ 4.8675,	„ 57.56

The portion (1), which, being the last, is in one sense likely to be the most homogeneous, corresponds to the relationship



The portions (2) and (3) would indicate as much as 0.7 molecule less of water.

§ 62. *Bromide of Ammonium*.—This salt separates as a cryohydrate from a saturated solution at  $-17^{\circ}\text{C}$ . Its formation is well marked, and its analysis was satisfactory. Of the final portion, 4.2591 grms. gave 1.3680 of  $\text{NH}_4\text{Br}$ . Of the immediately preceding crop of crystals, 5.5990 grms. gave 1.8010 of  $\text{NH}_4\text{Br}$ . The percentages are 32.12 and 32.17 respectively: these numbers correspond to the relationship



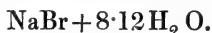
§ 63. Taking the value of the cryohydrate of chloride of ammonium from § 56 as  $\text{NH}_4\text{Cl} + 12.4\text{H}_2\text{O}$ , we have for the halogen salts of ammonium:—

	Solidifying-temperature of cryohydrate.	Number of molecules of water to 1 of salt.
$\text{NH}_4\text{I}$ . . . .	$-27.5$	6.4
$\text{NH}_4\text{Br}$ . . . .	$-17$	11.1
$\text{NH}_4\text{Cl}$ . . . .	$-16$	12.4

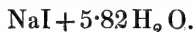
whence it is gathered that the relative faculties of chlorine, bromine, and iodine, in depressing the temperature at which the cryohydrates are formed, are similar with ammonium to their

faculties with potassium; namely, with both, iodine gives a lower-solidifying cryohydrate than bromine, and bromine lower than chlorine; and we have here also confirmation of the rule that in the same series the aquavalents diminish with the temperature of solidification.

§ 64. *Bromide of Sodium*.—To complete this series I take now the halides of sodium. The bromide of sodium separates from a saturated solution as a cryohydrate at  $-24^{\circ}$  C. Taking the last and the next to the last portions, 7.5010 grms. of the former gave 3.1000 of anhydrous bromide; of the latter, 8.3160 grms. gave 3.4605 of NaBr. The corresponding percentages are 41.33 and 41.61, the first of which indicates 8.12 and the second 8.08 molecules of water to 1 of the salt.



§ 65. *Iodide of Sodium*.—A saturated solution of iodide of sodium presents in the most remarkable manner the phenomenon of supersaturation. It may be cooled to  $-22^{\circ}$ , freely exposed to the air, and shaken without solidifying. On being placed in contact with solid carbonic acid and ether, it solidifies, and its temperature instantly rises to  $-15^{\circ}$ . The solidification once started by this extreme cold, the temperature remains constant at  $-15^{\circ}$ . Fragments of the cryohydrate so formed induce solidification in other portions subjected to the ice-salt cryogen. The last two portions were analyzed. Of the very last, 6.4000 grms. gave 3.8050 of NaI, or 59.45 per cent. Of the next to the last, 10.2450 grms. gave 6.0845, or 59.39 per cent. The molecular ratio of the cryohydrate is accordingly



Correlating the iodide and bromide of sodium with the chloride, we have, therefore,

	Solidifying-temperature of cryohydrate.	Number of molecules of water to 1 of salt.
NaI . .	$-15$	5.82
NaBr . .	$-24$	8.12
NaCl . .	$-23$	10.5

§ 66. It appears that the iodide of sodium forms the first exception we have yet met with to the general rule; for while its solidifying-point is above that of its companions, it attaches to itself a less number of water-molecules. In the Table below the whole nine combinations are shown; and they are there arranged according to the number of molecules of attached water, or in what might be called their "aquavalents" if this expression were

not too symphonous with "equivalents." Say, therefore, "water-worths."

Salt.	Temperature of solidification of cryohydrate.	Water-worth.
NaI . . . .	—15	5·8
NH <sub>4</sub> I . . . .	—27	6·4
NaBr . . . .	—24	8·2
KI . . . .	—23	8·5
NaCl . . . .	—23	10·5
NH <sub>4</sub> Br . . . .	—17	11·1
NH <sub>4</sub> Cl . . . .	—16	12·4
KBr . . . .	—13	14·0
KCl . . . .	—11·4	16·5

It appears that, for the same halogen, a sodium salt attaches less water than an ammonium salt, and the ammonium salt less than the potassium salt. Also, for the same metal, an iodine salt attaches less water than the bromine salt, and the latter less than the chlorine salt.

Or if we denote by  ${}^w\text{XM}$  the number of molecules of water attached to one molecule of XM, then

$${}^w\text{X Na} < {}^w\text{X NH}_4 < {}^w\text{XK},$$

and

$${}^w\text{IM} < {}^w\text{BrM} < {}^w\text{ClM}.$$

This remarkable rule has no exception amongst the above nine salts; and the only exception to the general rule, that the lower the solidifying-point the fewer the molecules of associated water, is offered by the iodide of sodium. Concerning this see § 68.

§ 67. It may be perhaps more than accidental that the numbers of molecular water-worths show a distinct tendency to be multiples of 0·5. For my own part, recognizing the possible range of analytical error, I for the present distinctly forbear to express any opinion as to whether we are here dealing with the same physical force which constitutes chemical attraction, and which regulates the integral ratios of molecular combination as most chemists appear to understand the term—or whether it is a distinct or distinctly conditioned force binding the salt and water together in quite a new ratio, or a ratio which can only be brought to the chemical one by multiplication by constants, at present arbitrary.

It is useful, however, to reflect that almost innumerable instances are known in which the molecular ratio between a salt and its ordinary water of crystallization is not a simple one. On examining the published determinations of water of crystallization effected by the chemists who are or have been both ac-

curate and scrupulous, we find that in many cases a less simple numerical ratio between the salt and its water would often correspond with the derived result far better than the ratio which has been thence deduced.

§ 68. With regard to the solidifying-point of the cryohydrate of iodide of sodium, I may here at once mention the exceedingly interesting fact which will be discussed in its proper place, that while the cold of a cryogen formed by mixing with ice any one of the other of these eight salts is so closely near as to be considered identical with the solidifying point of the corresponding cryohydrate, the cold of a freezing-mixture consisting of ice and iodide of sodium far exceeds  $-15^{\circ}$ , and in fact reaches  $-28^{\circ}$ , nearly the lowest temperature which I have yet got. On this ground it would be really entitled to be placed at the head of the list of the nine, where its water-worth has placed it in Table (§ 66).

§ 69. *Speculation concerning NaI.*—It is clear that when a freezing-mixture is in action, the liquid portion is a solution of the salt of such a strength that it resists solidification at the temperature of the mixture. Accordingly there must be a cryohydrate of sodium which remains liquid down to  $-28^{\circ}$ . Is its crystalline form so peculiar as not to respond by solidification to any solid particles in the air, and so to be an exceptionally persistent instance of supersaturation? Perhaps the cryohydrate can only exist in the liquid form. When it loses heat, it does not solidify as a whole, but in two parts, each of which is less soluble than the two together. For this reason the mixed solid separated would in all its stages have the same composition as the simple cryohydrate, while its separation, when once begun, might keep itself in activity. The heat-tension then exhibited would be the mean of the temperatures due to the solidification of each constituent.

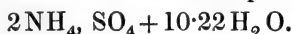
I can scarcely assert that this is a satisfactory or even to my own mind a clear explanation of the phenomenon. The difficulty would be to some extent removed if we could get evidence of an intermediate cryohydrate resembling that which exists with NaCl. Of such a cryohydrate I have no substantial evidence to offer at present.

#### *Cryohydrates of Alkaline Sulphates.*

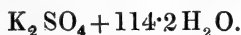
To see whether the noticeable relation between sodium, ammonium, and potassium is valid in other compounds of these metals, their sulphates were examined.

§ 70. *Sulphate of Ammonium.*—This body, when dissolved to saturation in water, yields abundantly the ordinary hydrated sulphate of ammonium when cooled to  $0^{\circ}$  C. The separation

stops shortly below  $0^{\circ}$  C.; and the solution may be cooled to  $-22^{\circ}$  while the liquid remains quite clear. This possible depression of the temperature in presence of one hydrate is clearly a happy incident in the genesis of the cryohydrate as far as the assurance of the freedom of the latter from the former is concerned. On cooling by means of carbonic acid and ether, solidification ensues shortly below  $-22^{\circ}$ , and the temperature rises to  $-17^{\circ}$ , at which it remains constant. Of the portion last to solidify, 7.0105 grms. on evaporation to dryness and heating to  $130^{\circ}$ , gave 2.9280 of  $2\text{NH}_4\text{SO}_4$ , or 41.7 per cent. Of the immediately preceding portion, 4.0695 grms. gave 1.7195, or 42.2 per cent. The first of these corresponds to the relation



71. *Sulphate of Potassium*.—The saturated solution of this salt solidifies at  $-1^{\circ}.2$ . Of the last portion, 3.9095 grms. yielded 0.3075, or 7.8 per cent. of  $\text{K}_2\text{SO}_4$ . Of the immediately preceding part, 5.2905 grms. gave 0.3960, or 7.5 per cent. The first of these shows the molecular relation



§ 72. *Sulphate of Sodium*.—This was examined in § 26. Its cryohydrate is formed at  $-0^{\circ}.7$ . The percentage of  $\text{Na}_2\text{SO}_4$  in the last portion was found to be 4.55, and the water-worth 165.6.

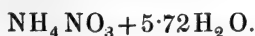
§ 73. Accordingly we have the sulphates of the alkalies arranged as follows:—

	Temperature of solidification of cryohydrate.	Water-worth.
$2\text{NH}_4\text{SO}_4$ . . .	$-17^{\circ}$	10.2
$\text{K}_2\text{SO}_4$ . . .	$-1^{\circ}.2$	114.2
$\text{Na}_2\text{SO}_4$ . . .	$-0^{\circ}.7$	165.6

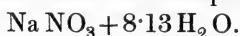
Once more, therefore, the lower the temperature of solidification of the cryohydrate, the less is its water-worth. But the order is different with  $\text{SO}_4$  from the order with a halogen.

#### *Nitrates of the Alkalies.*

§ 74. *Nitrate of Ammonium*.—The nitrate of ammonium separates as a cryohydrate from a saturated solution at  $-17^{\circ}.2$  in exceedingly beautiful fern-like crystals. Dried at  $100^{\circ}$  C. and heated to incipient fusion, 7.6100 grms. of the part last to solidify gave 3.3265 of the anhydrous salt. Of the next to the last, 7.2755 grms. gave 3.1475. The former therefore contained 43.71 per cent. of  $\text{NH}_4\text{NO}_3$ , the latter 43.26. The first indicates the relation

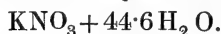


§ 75. *Nitrate of Sodium*.—The temperature at which this cryohydrate is formed was found by experiment to be  $-17^{\circ}5$ ; but, for reasons partly considered in § 69, I believe this temperature to be too low, and that, when supersaturation does not intervene, the temperature is  $-16^{\circ}5$ . Here, however, I assign to it the temperature got by direct observation. Of the last portion to solidify, 5·4210 grms. gave 2·2140 of  $\text{NaNO}_3$ , or 40·8 per cent., which indicates the composition



Of the previous crop of crystals, 6·9820 grms. gave 2·8850 of  $\text{NaNO}_3$ .

§ 76. *Nitrate of Potassium*.—This was examined in § 24. The cryohydrate solidifies at  $-2^{\circ}6$ , and contains 11·2 per cent. of nitre. The water-worth is expressed by the relation



§ 77. The nitrates of the alkalies therefore arrange themselves as follows:—

	Temperature of solidification of cryohydrate.	Water-worth.
$\text{NH}_4\text{NO}_3$ . . .	$-17\cdot2$	5·72
$\text{NaNO}_3$ . . .	$-17\cdot5$ (16·5)	8·13
$\text{KNO}_3$ . . .	$-2\cdot6$	44·6

I believe that here again the water-worth really falls with the temperature of solidification. But the order of the salts in regard to their water-worths is again different from the order observed with the sulphate, as well as from that of the chlorides of the same metals.

[To be continued.]

XXV. *General Theorems relating to Equilibrium and Initial and Steady Motions.* By LORD RAYLEIGH, M.A., F.R.S.\*

IF a material system start from rest under the action of given impulses, the energy of the actual motion exceeds that of any other which the system might have been guided to take by the operation of mere constraints; and the difference is equal to the energy of the motion which must be compounded with either to produce the other (Bertrand). A proof of this interesting theorem is given in Thomson and Tait's 'Natural Philosophy,' § 311—by a slight modification of which a more general result may be arrived at, giving rise to important corollaries.

Let P, Q, R denote the components of impulse on the particle  $m$ , and  $\dot{x}$ ,  $\dot{y}$ ,  $\dot{z}$  the component velocities assumed. Then, if

\* Communicated by the Author.

$\dot{x}', \dot{y}', \dot{z}'$  denote any other velocities consistent with the connexions of the system, the Principle of Virtual Velocities gives

$$\Sigma \{ (P - m\dot{x})\dot{x}' + (Q - m\dot{y})\dot{y}' + (R - m\dot{z})\dot{z}' \} = 0, \quad (1)$$

by means of which the initial velocities  $\dot{x}$  &c. are completely determined.

In equation (1) the hypothetical velocities  $\dot{x}'$  &c. are any whatever consistent with the constitution of the system; but if they are limited to be such as the system could acquire under the operation of the given impulses with the assistance of mere constraints, we have

$$2T' = \Sigma m(\dot{x}'^2 + \dot{y}'^2 + \dot{z}'^2) = \Sigma (P\dot{x}' + Q\dot{y}' + R\dot{z}'). \quad (2)$$

This includes the case of the actual motion.

Returning now to the general case, suppose that  $E'$  denotes the function

$$E' = \Sigma (P\dot{x}' + Q\dot{y}' + R\dot{z}') - \frac{1}{2} \Sigma m(\dot{x}'^2 + \dot{y}'^2 + \dot{z}'^2), \quad (3)$$

becoming for the actual motion

$$E = T = \frac{1}{2} \Sigma m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \quad (4)$$

or, for any motion of the kind considered in (2),

$$E' = T' = \frac{1}{2} \Sigma m(\dot{x}'^2 + \dot{y}'^2 + \dot{z}'^2). \quad (5)$$

For the difference between  $E'$  and  $E$  in (3) and (4), we get

$$E - E' = \frac{1}{2} \Sigma m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{1}{2} \Sigma m(\dot{x}'^2 + \dot{y}'^2 + \dot{z}'^2) - \Sigma (P\dot{x}' + Q\dot{y}' + R\dot{z}'),$$

in which by (1),

$$\Sigma (P\dot{x}' + Q\dot{y}' + R\dot{z}') = \Sigma m(\dot{x}\dot{x}' + \dot{y}\dot{y}' + \dot{z}\dot{z}');$$

so that

$$E - E' = \frac{1}{2} \Sigma m \{ (\dot{x} - \dot{x}')^2 + (\dot{y} - \dot{y}')^2 + (\dot{z} - \dot{z}')^2 \}, \quad (6)$$

which shows that  $E$  is a maximum for the actual motion (in which case it is equal to  $T$ ), and exceeds any other value  $E'$  by the energy of the difference of the real and hypothetical motions. From this we obtain Bertrand's theorem, if we introduce the further limitation that the hypothetical motion is such as the system can be guided to take by mere constraints; for then by (5)

$$E - E' = T - T'.$$

By means of the general theorem (6) we may prove that the energy due to given impulses is increased by any diminution (however local) in the inertia of the system. For whatever the motion acquired by the altered system may be, the value of  $E$

corresponding thereto (viz.  $T$ ) is greater than if the velocities had remained unchanged; and this, again, is evidently greater than the actual  $E$  (viz.  $T$ ) of the original motion. The total increase of energy is equal to the decrease which the alteration of mass entails in the energy of the former motion, together with the energy (under the new conditions of the system) of the difference of the old and new motions. If the change be small, the latter part is of the second order.

On the other hand, of course, any addition to the mass lessens the effect of the given impulses.

A similar deduction may be made from Thomson's theorem, which stands in remarkable contrast with that above demonstrated. The theorem is, that if a system be set in motion with prescribed velocities by means of applied forces of corresponding types, the whole energy of the motion is *less* than that of any other motion fulfilling the prescribed velocity-conditions. "And the excess of the energy of any other such motion, above that of the actual motion, is equal to the energy of the motion which would be generated by the action alone of the impulse which, if compounded with the impulse producing the actual motion, would produce this other supposed motion." From this it follows readily that, with given velocity-conditions, the energy of the initial motion of a system rises and falls according as the inertia of the system is increased or diminished\*.

We now pass to the investigation of some statical theorems which stand in near relation to the results we have just been considering. The analogy is so close that the one set of theorems may be derived from the other almost mechanically by the substitution of "force" for "impulse," and "potential energy of deformation" for "kinetic energy of motion." A similar mode of demonstration might be used but it will be rather more convenient to employ generalized coordinates.

Consider then a system slightly displaced by given forces from a position of stable equilibrium, from which configuration the coordinates are reckoned. The potential energy of the displacement  $V$  is a quadratic function of the coordinates  $\psi_1, \psi_2$  &c.

$$V = \frac{1}{2} a_{11} \psi_1^2 + \frac{1}{2} a_{22} \psi_2^2 + \dots + a_{12} \psi_1 \psi_2 + a_{23} \psi_2 \psi_3 + \dots \quad (7)$$

If, then,

$$E' = \Psi_1 \psi'_1 + \Psi_2 \psi'_2 + \dots - V', \quad \dots \quad (8)$$

where  $\Psi_1, \Psi_2$ , &c. are the forces,  $E'$  will be an absolute maximum for the position actually assumed by the system. In equation (8),  $V$  is to be understood merely as an abbreviation

\* See a paper by the author on Resonance, Phil. Trans. 1871, p. 94.



for the right-hand member of (7), and the displacements  $\psi_1$  &c. are any whatever.

In the position of equilibrium, since then  $\Psi_1 = \frac{dV}{d\psi_1}$  &c.,

$$E = V = \frac{1}{2}(\Psi_1\psi_1 + \dots); \quad \dots \quad (9)$$

and thus

$$\begin{aligned} E - E' &= \frac{1}{2}(\Psi_1\psi_1 + \dots) + V' - (\Psi'_1\psi'_1 + \dots) \\ &= \frac{1}{2}\Psi_1(\psi_1 - \psi'_1) + \dots + V' - \frac{1}{2}(\Psi'_1\psi'_1 + \dots). \end{aligned}$$

Now, by a reciprocal property readily proved\*,

$$\Psi_1\psi'_1 + \dots = \Psi'_1\psi_1 + \dots, \quad \dots \quad (10)$$

and also

$$V' = \frac{1}{2}\Psi'_1\psi'_1 + \dots, \quad \dots \quad (11)$$

where  $\Psi'_1$  &c. is the set of forces necessary to maintain the configuration  $\psi'_1$  &c. Thus by (10) and (11),

$$E - E' = \frac{1}{2}(\Psi_1 - \Psi'_1)(\psi_1 - \psi'_1) + \dots, \quad \dots \quad (12)$$

a positive quantity representing the potential energy of the deformation  $(\psi_1 - \psi'_1)$  &c. Thus  $E'$  attains its greatest value  $E$  in the case of the actual configuration, and the excess of this value  $E$  over any other is the potential energy of the displacement which must be compounded with either to produce the other. So far the displacement represented by  $\psi'_1$  &c. is any whatever; but if we confine ourselves to displacements due to the given forces and differing from the actual displacements only by reason of the introduction of constraints limiting the freedom of the system, then  $E' = V'$ ; and the theorem as to the maximum value of  $E'$  may be stated with the substitution of  $V'$  for  $E'$ . Thus the introduction of a constraint has the effect of diminishing the potential energy of deformation of a system acted on by given forces; and the amount of the diminution is the potential energy of the difference of the deformations.†

For an example take the case of a horizontal rod clamped at one end and free at the other, from which a weight may be suspended at the point  $Q$ . If a constraint is applied holding a point  $P$  of the rod in its place (*e. g.* by a support situated under it), the potential energy of the bending due to the weight at  $Q$  is less than it would be without the constraint by the potential energy of the difference of the deformations.

\* By substituting  $\Psi_1 = \frac{dV}{d\psi_1}$  &c.,  $\Psi'_1 = \frac{dV'}{d\psi'_1}$  &c.

† Compare Maxwell's 'Theory of Heat,' p. 131.

And since the potential energy in either case is proportional to the descent of the point Q, we see that the effect of the constraint is to diminish this descent.

The theorem under consideration may be placed in a clearer light by the following interpretation of the function E.

In forming the conditions of equilibrium, we are only concerned with the forces which act upon the system when in that position; but we may, if we choose, attribute any consistent values to the forces for other positions. Suppose, then, that the forces are constant, as if produced by weights. Then, in any position, E denotes the work, positive or negative, which must be done upon the system in order to bring it into the configuration defined by  $V=0$ . Thus, to return to the rod with the weight suspended from Q, E represents the work which must be done in order to bring the rod from the configuration to which E refers into the horizontal position. And this work is the difference between the work necessary to raise the weight and that gained during the unbending of the rod. Further, if the configuration in question is one of equilibrium with or without the assistance of a constraint (such as the support at P), the work gained during the unbending is exactly the half of that required to raise the weight; so that E is the same as the potential energy of the bending, or *half* the work required to raise the weight.

When the rod, unsupported at P, is bent by the weight at Q, the point P drops. The energy of the bending is the same as the total work required to restore the rod to a horizontal position. Now this restoration may be effected in two steps. We may first, by a force applied at P, raise that point into its proper position, a process requiring the expenditure of work. The system will now be in the same condition as that in which it would have been found if the point P had been originally supported; and therefore it requires less work to restore the configuration  $V=0$  when the system is under constraint than when it is free. Accordingly the potential energy of deformation is also less in the former case.

We may now prove that any relaxation in the stiffness of a system equilibrated by given forces is attended by an *increase* in the potential energy of deformation. For if the original configuration be maintained, E will be greater than before, in consequence of the diminution in the energy of a given deformation. *A fortiori*, therefore, will E be greater when the system adjusts itself to equilibrium, when the value of E is as great as possible. Conversely, any increase in V as a function of the coordinates entails a diminution in the actual value of V corresponding to equilibrium. Since a loss of freedom may be

regarded as an increase of stiffness, we see again how it is that the introduction of a constraint diminishes  $V$ .

The statical analogue of Thomson's theorem for initial motions refers to systems in which given deformations are produced by the necessary forces of corresponding types—for example, the rod of our former illustration, of which the point  $P$  is displaced through a given distance, as might be done by raising the support situated under it. The theorem is to the effect that the potential energy  $V$  of a system so displaced and in equilibrium is as small as it can be under the circumstances, and that the energy of any other configuration exceeds this by the energy of that configuration which is the difference of the two.

To prove this, suppose that the conditions are that  $\psi_1, \psi_2, \psi_3, \dots \psi_r$  are given, while the forces of the remaining types  $\Psi_{r+1}, \Psi_{r+2}, \&c.$  vanish. The symbols  $\psi_1, \&c., \Psi_1, \&c.$  refer to the actual equilibrium-configuration, and  $\psi_1 + \Delta\psi_1, \psi_2 + \Delta\psi_2, \&c., \Psi_1 + \Delta\Psi_1, \Psi_2 + \Delta\Psi_2, \&c.$  to any other configuration subject to the same *displacement*-conditions. For each suffix, therefore, *either*  $\Delta\psi$  *or*  $\Delta\Psi$  vanishes. Now for the potential energy of the hypothetical deformation we have

$$\begin{aligned} 2(V + \Delta V) &= (\Psi_1 + \Delta\Psi_1)(\psi_1 + \Delta\psi_1) + \dots \\ &= 2V + \Psi_1\Delta\psi_1 + \Psi_2\Delta\psi_2 + \dots \\ &\quad + \Delta\Psi_1 \cdot \psi_1 + \Delta\Psi_2 \cdot \psi_2 + \dots \\ &\quad + \Delta\Psi_1 \cdot \Delta\psi_1 + \Delta\Psi_2 \cdot \Delta\psi_2 + \dots \quad (13) \end{aligned}$$

But by the reciprocal relation,

$$\Psi_1 \cdot \Delta\psi_1 + \Psi_2 \cdot \Delta\psi_2 + \dots = \Delta\Psi_1 \cdot \psi_1 + \Delta\Psi_2 \cdot \psi_2 + \dots,$$

of which the former by hypothesis is zero. Thus

$$2\Delta V = \Delta\Psi_1 \cdot \Delta\psi_1 + \Delta\Psi_2 \cdot \Delta\psi_2 + \dots, \quad (14)$$

as was to be proved.

The effect of a relaxation in stiffness must clearly be to diminish  $V$ ; for such a diminution would ensue if the configuration remained unaltered, and therefore still more when the system returns to equilibrium under the altered conditions. It will be understood that in particular cases the diminution spoken of may vanish.

The connexion between the two statical theorems, dealing respectively with systems subject to given displacements and systems displaced by given forces, will be perhaps brought out more clearly by another demonstration of the latter. We have to show that the removal of a constraint is attended by an increase in the potential energy of deformation. By a suitable choice of coordinates the conditions of constraint may be

expressed by the vanishing of the first  $r$  coordinates  $\psi_1 \dots \psi_r$ . The relation of the two cases to be compared is expressed by supposing the forces of the remaining types  $\Psi_{r+1}, \dots$  to be the same, so that  $\Delta\Psi_{r+1}$  &c. vanish. Thus for every suffix either  $\psi$  vanishes or else  $\Delta\Psi$ . Accordingly  $\Sigma\psi\Delta\Psi$  is zero, and therefore also, by the law of reciprocity,  $\Sigma\Psi\Delta\psi$ . Hence, as above,

$$2\Delta V = \Sigma\Delta\Psi\Delta\psi, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

showing that the removal of the constraint increases the potential energy by the potential energy of the difference of the deformations.

Corresponding to the above theorems for  $T$  and  $V$ , there are two more relating to the function  $F$  introduced by me in a paper printed in the 'Proceedings of the Mathematical Society' for June 1873, expressing the effects of viscosity. We have here to consider systems destitute both of kinetic and potential energy, of which probably the best example is a combination of electrical conductors, conveying currents, whose inductive effects, dependent on inertia, may be neglected. The equations giving the magnitudes of the steady currents are of the form

$$\frac{dF}{d\dot{\psi}} = \Psi, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where  $F$  is a quadratic function (in this case with constant coefficients) of the velocities  $\dot{\psi}$ , &c., representing half the dissipation of energy in the unit of time, and  $\Psi$ , &c. are the electromotive forces. It is scarcely necessary to go through the proofs, as they are precisely similar to those already given with the substitution of  $F$  for  $T$ , and steady forces for impulses. The analogue of Bertrand's theorem tells us that, if *given electromotive forces* act, the development of heat in unit time is diminished by the introduction of any constraint, as, for example, breaking one of the contacts. And by comparison with Thomson's theorem for initial motions we learn that, if *given currents* be maintained in the system by forces of corresponding types, the whole development of heat is the least possible under the circumstances (Maxwell's 'Electricity and Magnetism,' § 284). And precisely as before, we might deduce corollaries relating to the effect of altering the resistance of any part of the combination.

XXVI. *Notices respecting New Books.*

*Exposition Géométrique des Propriétés Générales des Courbes.* Par CHARLES RUCHONNET (*de Lausanne*). *Troisième édition, augmentée et en partie refondue.* Paris: Gauthier-Villars. Lausanne: Georges Bridel. Zurich: Orell, Fuessli et Comp. 1874 (8vo, pp. 160).

THIS work contains a very complete account of the properties of curved lines which may be considered general, as distinguished from those possessed by certain curves at individual or singular points. Though the author has occasion to notice that there may be points of inflection, he does not consider them, as inflection cannot be a property enjoyed by the points of a curve generally. Thus the proof of art. 44, that in general a curve cuts its osculating plane at the point of contact, consists in showing that if the curve do not cut the osculating plane at an assigned point, there must be inflection at the corresponding point of another curve.

The consequence of this is, that the book consists mainly of a discussion of curvature, and of the properties of the osculating circle and of allied subjects. Thus the five sections which make up the first part of the work (that devoted to plane curves) treat of the tangent, curvature, the osculating circle, and expressions for different magnitudes: viz. (1) those which arise out of a consideration of an infinitely small arc and the tangents at its extremities, such as that the difference between the arc and its chord ultimately equals one 24th of the square of the angle of contingence multiplied by the length of the arc; (2) those which depend on the difference between the radii of curvature at two infinitely near points of the curve, such as that the difference between the angles contained by the chord and the tangents at its extremities is ultimately equal to one half of the square of the angle of contingence multiplied by  $\frac{d\rho}{ds}$ .

In the second part (that devoted to tortuous curves, and which occupies about three quarters of the volume) the subjects are much the same; but, of course, many more points come under notice; and, besides, there is an account of Ruled and Developable Surfaces, sufficient to enable the reader to understand the properties of the polar and rectifying surfaces of these curved lines.

Our author's treatment of the subject as a whole is both minute and exact; and though we do not profess to be acquainted with the whole literature of the subject, it is only fair to say that we do not know any work which contains an account of it to be compared with that before us in completeness. The chief peculiarity, however, of the treatment is in its method, which is wholly that of limits—each proposition being separately proved by reasoning directly from a diagram, without the use of any of the elementary formulæ of the differential calculus. Thus nothing so recondite

*Phil. Mag.* S. 4. Vol. 49. No. 324. *Maech* 1875. R

as Taylor's Theorem is employed from one end of the book to the other, though the author comes rather near to using it in art. 46. It is unnecessary to add that such a treatment of this subject requires considerable powers of geometrical exposition; and these are certainly possessed by the author. In fact he gives us to understand that he has worked out the whole subject from his own point of view with not much more aid from the labours of his predecessors than what is implied in the fact of their having established by a different method all the leading facts of the subject.

The advantage gained by a purely geometrical exposition of such a subject as Curvature is, that the student learns from it what in actual space corresponds to his algebraical formulæ; and this is a matter to which his attention has often to be directed. On the other hand, it is liable to the somewhat serious drawback, that the results are obtained by the use of an instrument of research inadequate to the purpose, unless in a very skilful hand, while they can easily be got at by other means. Suppose a student to have a moderate skill in analysis, and to know the few general formulæ relating to the subject which are to be found in all books of solid geometry; *e. g.*, suppose him to have mastered pp. 407–417 of De Morgan's 'Differential Calculus,' it is hardly too much to affirm that he would find it easier to investigate by their means most of the theorems contained in M. Ruchonnet's book than to make out his proofs. He would observe that such magnitudes as the angles of contingence and torsion, the radius of curvature, the ratio of its increment to that of the arc— $\frac{dp}{ds}$  in fact—are intrinsic

to the curve, and the relations between them independent of the coordinate axes chosen. Consequently he would choose the axes so as to simplify, as much as possible, the general expressions given in books; and, as a rule, the required results would then be obtained without much difficulty. Take for instance the proposition quoted above, that in general the curve cuts the osculating plane at the point of contact. Suppose the curve to be given by the equations  $y=F(x)$  and  $z=f(x)$ , that the point under consideration is taken as the origin, the osculating plane as the plane of  $xy$ , and (though this is not necessary for the purpose immediately in hand) the tangent as the axis of  $x$ . It follows from these suppositions that  $F(0)$ ,  $F'(0)$ ,  $f(0)$ ,  $f'(0)$ , and  $f''(0)$  are severally zero. Now consider a point  $(h, k, l)$  near the origin; we have

$$k=F(h)=\frac{1}{2}F''(0) \cdot h^2 + \frac{1}{6}F'''(0) \cdot h^3 + \dots,$$

$$l=f(h)=\frac{1}{6}f'''(0) \cdot h^3 + \frac{1}{24}f''''(0) \cdot h^4 + \dots$$

The second equation shows that in general  $l$  changes its sign with  $h$ , i. e. on one side of the normal plane the curve is above, and on the other side below the osculating plane, which it therefore cuts at the point of contact. Our author's proof of this theorem is most ingenious, but, as already mentioned, is indirect, and by no means easy to follow.

As a further illustration of our meaning we will consider a property of plane curves, which is not noticed in the usual text-books, and which M. Ruchonnet attributes to M. Abel Transon (p. 42); viz. that if  $\theta$  is the angle between the normal and the diametral curve at the same point of a given curve,

$$\tan \theta = \frac{1}{3} \cdot \frac{d\rho}{ds}.$$

Let  $y=f(x)$  be the equation to the curve, the point under consideration (O) being taken as the origin, and the axis of  $x$  so chosen as to touch the curve; consequently  $f(0)$  and  $f'(0)$  are severally zero. Suppose the curve to be cut by a chord PP' parallel to Ox; if A is its middle point, the ultimate value of AOy is  $\theta$ . If  $(h, k)$  and  $(-h', k)$  are the coordinates of P and P', it is plain that  $\tan \theta$  is the ultimate value of  $(h-h') \div 2k$ . Now, observing that it is not necessary to retain terms above the third order, we have

$$k=f(h) = \frac{1}{2}f''(0) \cdot h^2 + \frac{1}{6} \cdot f'''(0) \cdot h^3,$$

and  $k=f(-h) = \frac{1}{2}f''(0) \cdot h'^2 - \frac{1}{6} \cdot f'''(0) \cdot h'^3.$

Hence 
$$h^2 = \frac{2k}{f''(0)} \left\{ 1 - \frac{1}{3} \cdot \frac{f'''(0)}{f''(0)} \cdot h \right\},$$

and 
$$h'^2 = \frac{2k}{f''(0)} \left\{ 1 + \frac{1}{3} \cdot \frac{f'''(0)}{f''(0)} \cdot h' \right\}.$$

Therefore, subtracting and dividing out  $h+h'$ , the ultimate value of  $\frac{h-h'}{2k}$  is  $-\frac{1}{3} \cdot \frac{f'''(0)}{\{f''(0)\}^2}$ . But it follows, from the well-known general

expression for the radius of curvature, that  $-\frac{f'''(0)}{\{f''(0)\}^2}$  is the value  $\frac{d\rho}{ds}$  at the origin; and this proves the theorem.

*Éléments de Calcul Approximatif.* Par CHARLES RUCHONNET (*de Lausanne*). *Seconde édition augmentée.* Paris: Gauthier-Villars. Lausanne: Georges Bridel. Zurich: Orell, Fuessli et Comp. 1874 (8vo, pp. 65).

The question discussed in the work before us is this:—What precautions must be taken in a numerical operation to ensure that the first  $n$  digits of the final result shall be exact? The author considers separately the operations of addition (and subtraction), multiplication, division, extraction of roots, and, very briefly, the case of a function of one variable. He illustrates his rule by working out several examples; but he does not insert examples for practice, as an English writer would probably have done. The above-mentioned operations become complicated when any or all the numbers concerned are incommensurable; and in these cases a second question arises, viz. to what degree of approximation these numbers must be taken separately to ensure the required degree of accuracy in the final result.

We shall perhaps convey the best idea of the book by descri-

bing briefly our author's treatment of the question of multiplication, to which his third chapter is devoted. In the first place he explains, by means of two examples, Oughtred's method of contracted multiplication; but instead of leaving the last figure uncertain as is usually done, he notices that the process gives an approximation *in defect*, and points out that if the sum of the digits in the multiplier, which give partial products, be increased by the first unused digit of the multiplier, and by unity if there be a second unused digit in the multiplier, and then this sum be added to the product, we now have an approximation *in excess*; and by comparing the two we obtain a result in which a certain number of digits are known to be exact. Moreover the rule, as usually stated, directs that if, for instance, the result were required to be true for two places of decimals, the unit digit of the multiplier should be placed under the second decimal digit of the multiplicand; our author notices that it should usually be placed under the third decimal digit, and in certain circumstances under the fourth or fifth, and so on in other cases. He next enters on the question, Given that the factors are incommensurable numbers, to what degree of approximation must they be known that the first  $n$  digits of the product may be exact? He first shows that when the factors are approximate *by defect*, the relative error of their product is less than the sum of the relative errors of the factors; and then reasons as follows:—Suppose that there are  $p$  factors ( $p$  being less than 10), calculate each factor to  $n+1$  digits; then the relative error of each factor is less than  $\frac{1}{p \cdot 10^n}$ , and consequently the sum

of their relative errors will be less than  $\frac{1}{10^n}$ , and their product will have the first  $n$  digits exact. He also observes that if the first digit of the required product is known before hand, it is, under certain circumstances (which he specifies), enough to calculate some of the factors to  $n$  digits.

It will be evident from this that the author is quite justified in thinking that "he has given completeness, in the present work, to methods laid down by other writers." He states that the work was originally published as an appendix to that on curved lines noticed above, that it has been carefully revised, and contains several important additions; amongst others is a complete solution of the question, How many digits of a number must be known in order that its  $m$ th root may have its first  $n$  digits exact?



XXVII. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

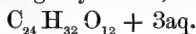
[Continued from p. 151.]

June 18, 1874.—Joseph Dalton Hooker, C.B., President, in the Chair.

THE following communication was read:—

“On Coniferine, and its Conversion into the Aromatic Principle of Vanilla.” By Ferd. Tiemann and Wilh. Haarmann.

The sap of the cambium of coniferous trees contains a beautiful crystalline glucoside, coniferine, which was discovered by Hartig and examined some years ago by Kubel, who arrived at the formula



A minute study of this compound leads us to represent the molecule of coniferine by the expression

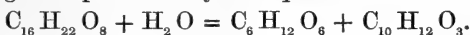


the percentages of which nearly coincide with the theoretical values of Kubel's formula.

Submitted to fermentation with emulsine, coniferine splits into sugar and a splendid compound, crystallizing in prisms which fuse at 73°. This body is easily soluble in ether, less so in alcohol, almost insoluble in water; its composition is represented by the formula



The change is represented by the equation

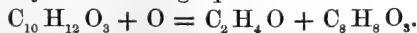


Under the influence of oxidizing agents the product of fermentation undergoes a remarkable metamorphosis. On boiling it with a mixture of potassium bichromate and sulphuric acid, there passes with the vapour of water, in the first place ethylic aldehyde, and subsequently an acid compound soluble in water, from which it may be removed by ether. On evaporating the ethereal solution, crystals in stellar groups are left behind, which fuse at 81°. These crystals have the taste and odour of vanilla. An accurate comparative examination has proved them to be identical with the crystalline substance which constitutes the aroma of vanilla, and which is often seen covering the surface of vanilla-rods.

On analysis, the crystals we obtained were found to contain

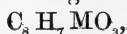


This is exactly the composition which recent researches of Carles have established for the aromatic principle of vanilla. The transformation of the crystalline product of fermentation into vanilline is represented by the following equation:—



To remove all doubt regarding the identity of artificial vanilline with the natural compound, we have transformed the former into

a series of salts which have the general formula



and into two substitution-products,



and

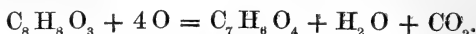


both of which had previously been prepared by Carles from the natural compound.

In order further to elucidate the nature of vanilline, we have submitted this body to fusion with alkali. The product of this action is a well-known acid discovered by Strecker, and described by him as protocatechuic acid,



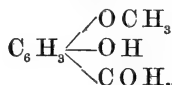
which is thus formed—



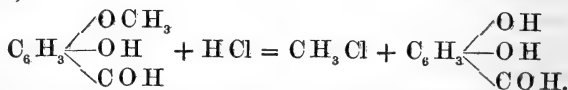
We have identified this substance by analysis, by the study of its reactions, and also by transforming it into pyrocatechine,  $\text{C}_6\text{H}_6\text{O}_2$ ,



The transformation into protocatechuic acid fixes the constitution of vanilline. This compound is the methylated aldehyde of protocatechuic acid; its composition referred to benzol is represented by the formula



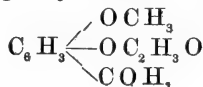
Indeed, submitted under pressure to the action of hydrochloric acid, vanilline splits into chloride of methyl and protocatechuic aldehyde,



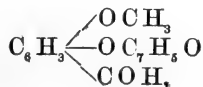
A corresponding action takes place with hydriodic acid; but in this case the aldehyde is destroyed.

An additional proof of the correctness of our view regarding the constitution of vanilline is obtained by treating this substance with acetic anhydride and benzoyl chloride.

The action does not go beyond the formation of the compounds

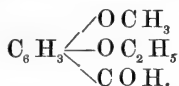


and

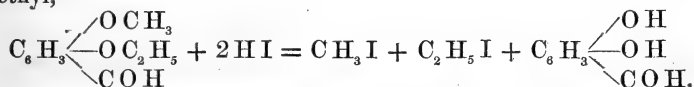


showing that vanilline does not contain more than one hydroxylic group.

The constitution of vanilline being thus made out, there could be no doubt regarding the structure of the product of fermentation from which vanilline arises. This compound is the ethylic ether of vanilline,



That such is the constitution of the body is proved by the simultaneous formation of ethylic aldehyde when vanilline is formed. We obtained, however, an additional confirmation of this conception by submitting the product of fermentation to the action of hydriodic acid under pressure, when an alcohol iodide was formed, which we succeeded in separating into the iodides of methyl and ethyl,



The experiments we have described in this note were performed in the laboratory of Professor A. W. Hofmann, to whom we are deeply indebted for the advice and assistance he has given us in the course of these researches.

June 11, 1874.—The following communications were read:—

“On the alleged Expansion in Volume of various Substances in passing by Refrigeration from the state of Liquid Fusion to that of Solidification.” By Robert Mallet, C.E., F.R.S.

Since the time of Réaumur it has been stated, with very various degrees of evidence, that certain metals expand in volume at or near their points of consolidation from fusion. Bismuth, cast iron, antimony, silver, copper, and gold are amongst the number, and to these have recently been added certain iron furnace-slugs. Considerable physical interest attaches to this subject from the analogy of the alleged facts to the well-known one that water expands between 39° F. and 32°, at which it becomes ice; and a more extended interest has been given to it quite recently by Messrs. Nasmyth and Carpenter having made the supposed facts, more especially those relative to cast iron and to slags, the foundation of their peculiar theory of lunar volcanic action as developed in their work, ‘The Moon as a Planet, as a World, and a Satellite’ (4to, London, 1874). There is considerable ground for believing that bismuth does expand in volume at or near consolidation; but with respect to all the other substances supposed to do likewise, it is the object of this paper to show that the evidence is insufficient, and that with respect to cast iron and to the basic silicates constituting iron slags, the allegation of their expansion in volume, and therefore that their density when molten is greater than when solid, is wholly erroneous. The determination of the specific gra-

vity, in the liquid state, of a body having so high a fusing temperature as cast iron is attended with many difficulties. By an indirect method, however, and operating upon a sufficiently large scale, the author has been enabled to make the determination with considerable accuracy. A conical vessel of wrought iron of about 2 feet in depth and 1.5 foot diameter of base, and with an open neck of 6 inches in diameter, being formed, was accurately weighed empty, and also when filled with water level to the brim; the weight of its contents in water, reduced to the specific gravity of distilled water at 60° F., was thus obtained. The vessel being dried was now filled to the brim with molten grey cast iron, additions of molten metal being made to maintain the vessel full until it had attained its maximum temperature (yellow heat in daylight) and maximum capacity. The vessel and its content of cast iron when cold were weighed again, and thus the weight of the cast iron obtained. The capacity of the vessel when at a maximum was calculated by applying to its dimensions at 60° the expansion calculated from the coefficient of linear dilatation, as given by Laplace, Riemann, and others, and from its range of increased temperature; and the weight of distilled water held by the vessel thus expanded was calculated from the weight of its contents when the vessel and water were at 60° F.

We have now, after applying some small corrections, the elements necessary for determining the specific gravity of the cast iron which filled the vessel when in the molten state, having the absolute weights of equal volumes of distilled water at 60° and of molten iron. The mean specific gravity of the cast iron which filled the vessel was then determined by the usual methods. The final result is that, whereas the specific gravity of the cast iron at 60° F. was 7.170, it was only 6.650 when in the molten condition; cast iron, therefore, is less dense in the molten than in the solid state. Nor does it expand in volume at the instant of consolidation, as was conclusively proved by another experiment. Two similar 10-inch spherical shells, 1.5 inch in thickness, were heated to nearly the same high temperature in an oven, one being permitted to cool empty as a measure of any permanent dilatation which both might sustain by mere heating and cooling again, a fact well known to occur. The other shell, when at a bright red heat, was filled with molten cast iron and permitted to cool, its dimensions being taken by accurate instruments at intervals of 30 minutes, until it had returned to the temperature of the atmosphere (53° F.), when, after applying various corrections, rendered necessary by the somewhat complicated conditions of a spherical mass of cast iron losing heat from its exterior, it was found that the dimensions of the shell, whose interior surface was in perfect contact with that of the solid ball which filled it, were, within the limit of experimental error, those of the empty shell when that also was cold (53° F.), the proof being conclusive that no expansion in volume of the contents of the shell had taken place. The central

portion was much less dense than the exterior, the opposite of what must have occurred had expansion in volume on cooling taken place.

It is a fact, notwithstanding what precedes, and is well known to ironfounders, that certain pieces of cold cast iron do float on molten cast iron of the same quality, though they cannot do so through their buoyancy. As various sorts of cast iron vary in specific gravity at 60° F., from nearly 7·700 down to 6·300, and vary also in dilatibility, some cast irons may thus float or sink in molten cast iron of different qualities from themselves through buoyancy or negative buoyancy alone; but where the cold cast iron floats upon molten cast iron of less specific gravity than itself, the author shows that some other force, the nature of which yet remains to be investigated, keeps it floating; this the author has provisionally called the repellent force, and has shown that its amount is, *cæteris paribus*, dependent upon the relation that subsists between the volume and "effective" surface of the floating piece. By "effective" surface is meant all such part of the immersed solid as is in a horizontal plane or can be reduced to one. The repellent force has also relations to the difference in temperature between the solid and the molten metal on which it floats.

The author then extends his experiments to lead, a metal known to contract greatly in solidifying, and, with respect to which, no one has suggested that it expands at the moment of consolidation. He finds that pieces of lead having a specific gravity of 11·361, and being at 70° F., float or sink upon molten lead of the same quality, whose calculated specific gravity was 11·07, according to the relation that subsists between the volume and the "effective" surface of the solid piece, thin pieces with large surface always floating, and *vice versâ*. An explanation is offered of the true cause of the ascending and descending currents observed in very large "ladles" of liquid cast iron, as stated by Messrs. Nasmyth and Carpenter. The facts are shown to be in accordance with those above mentioned, and when rightly interpreted to be at variance with the views of these authors.

Lastly, the author proceeds to examine the statements made by these writers, as to the floating of lumps of solidified iron furnace-slag upon the same when in a molten state; he examines the conditions of the alleged facts, and refers to his own experiments upon the total contraction of such slags, made at Barrow Iron-works (a full account of which he has given in his paper on "The true Nature and Origin of Volcanic Heat and Energy," printed in *Phil. Trans.* 1873), as conclusively proving that such slags are not denser in the molten than in the solid state, and that the floating referred to is due to other causes. The author returns thanks to several persons for facilities liberally afforded him in making these experiments.

"Spectroscopic Notes.—No. I. On the Absorption of great Thicknesses of Metallic and Metalloidal Vapours." By J. Norman Lockyer, F.R.S.

It has been assumed hitherto that a great *thickness* of a gas or

vapour causes its radiation, and therefore its absorption, to assume more and more the character of a continuous spectrum as the thickness is increased.

It has been shown by Dr. Frankland and myself that such a condition obtains when the *density* of a vapour is increased, and my later researches have shown that it is brought about in two ways. Generalizing the work I have already done, without intending thereby to imply necessarily that the rule will hold universally, or that it exhausts all the phenomena, it may be stated that metallic elements of low specific gravity approach the continuous spectrum by widening their lines, while metallic elements of high specific gravity approach the continuous state by increasing the number of their lines. Hence in the vapours of Na, Ca, Al, and Mg we have a small number of lines which broaden, few short lines being added by increase of density; in Fe, Co, Ni, &c. we have many lines which do not so greatly broaden, many short lines being added.

The observations I made in India during the total solar eclipse of 1871 were against the assumption referred to; and if we are to hold that the lines, both "fundamental" and "short," which we get in a spectrum, are due to atomic impact (defining by the word atom, provisionally, that mass of matter which gives us a line-spectrum), then, as neither the quantity of the impacts nor the quality is necessarily altered by increasing the thickness of the stratum, the assumption seems also devoid of true theoretical foundation.

One thing is clear, that if the assumed continuous spectrum is ever reached by increased thickness, as by increased density, it must be reached through the "short-line" stage.

To test this point I have made the following experiments :—

1. An iron tube about 5 feet long was filled with dry hydrogen; pieces of sodium were carefully placed at intervals along the whole length of the tube, except close to the ends. The ends were closed with glass plates. The tube was placed in two gas-furnaces in line and heated. An electric lamp was placed at one end of the tube and a spectroscope at the other.

When the tube was red-hot and filled with sodium-vapour throughout, as nearly as possible, its whole length, a stream of hydrogen slowly passing through the tube, the line D was seen to be absorbed; it was no thicker than when seen under similar conditions in a test-tube, and far thinner than the line absorbed by sodium-vapour in a test-tube, if the density be only slightly increased.

Only the longest "fundamental" line was absorbed.

*The line was thicker than the D line in the solar spectrum, in which spectrum all the short lines are reversed.*

2. As it was difficult largely to increase either the temperature or the density of the sodium-vapour, I have made another series of experiments with iodine-vapour.

I have already pointed out the differences indicated by the spectroscope between the quality of the vibrations of the "atom"

of a metal and of the "subatom" of a metalloid (by which term I define that mass of matter which gives us a spectrum of channelled spaces, and builds up the continuous spectrum in its own way). Thus, in iodine, the short lines, brought about by increase of density in an atomic spectrum, are represented by the addition of a system of well-defined "beats" and broad bands of continuous absorption to the simplest spectrum, which is one exquisitely rhythmical, the intervals increasing from the blue to the red, and in which the beats are scarcely noticeable.

On increasing the density of a very small thickness by a gentle heating, the beats and bands are introduced, and, as the density is still further increased, the absorption becomes continuous throughout the whole of the visible spectrum.

The absorption of a thickness of 5 feet 6 inches of iodine-vapour at a temperature of 59° F. has given me no indication of bands, while the beats were so faint that they were scarcely visible.

"Spectroscopic Notes.—No. II. On the Evidence of Variation in Molecular Structure." By J. Norman Lockyer, F.R.S.

1. In an accompanying note I have shown that when different degrees of dissociating power are employed the spectral effects are different.

2. In the present note I propose to give a preliminary account of some researches which have led me to the conclusion that, starting with a mass of elemental matter, such mass of matter is continually broken up as the temperature (including in this term the action of electricity) is raised.

3. The evidence upon which I rely is furnished by the spectroscopy in the region of the visible spectrum.

4. To begin by the extreme cases, all solids give us continuous spectra; all vapours produced by the high-tension spark give us line spectra.

5. Now the continuous spectrum may be, and as a matter of fact is, observed in the case of chemical compounds, whereas all compounds known as such are resolved by the high-tension spark into their constituent elements. We have a right, therefore, to assume that an element in the solid state is a more complex mass than the element in a state of vapour, as its spectrum is the same as that of a mass which is known to be more complex.

6. The spectroscopy supplies us with intermediate stages between these extremes.

(a) The spectra vary as we pass from the induced current with the jar to the spark without the jar, to the voltaic arc, or to the highest temperature produced by combustion. The change is always in the same direction; and here, again, the spectrum we obtain from elements in a state of vapour (a spectrum characterized by spaces and bands) is similar to that we obtain from vapours of which the compound nature is unquestioned.

(β) At high temperatures, produced by combustion, the vapours of some elements (which give us neither line- nor channelled space-

spectra at those temperatures, although we undoubtedly get line-spectra when electricity is employed, as stated in 4) give us a continuous spectrum at the more refrangible end, the less refrangible end being unaffected.

( $\gamma$ ) At ordinary temperatures, in some cases, as in selenium, the more refrangible end is absorbed; in others the continuous spectrum in the blue is accompanied by a continuous spectrum in the red. On the application of heat, the spectrum in the red disappears, that in the blue remains; and further, as Faraday has shown in his researches on gold-leaf, the masses which absorb in the blue may be isolated from those which absorb in the red. It is well known that many substances known to be compounds in solution give us absorption in the blue or blue and red; and, also, that the addition of a substance known to be compound (such as water) to substances known to be compound which absorb the blue, superadds an absorption in the red.

7. In those cases which do not conform to what has been stated the limited range of the visible spectrum must be borne in mind. Thus I have little doubt that the simple gases, at the ordinary conditions of temperature and pressure, have an absorption in the ultra-violet, and that highly compound vapours are often colourless because their absorption is beyond the red, with or without an absorption in the ultra-violet. Glass is a good case in point; others will certainly suggest themselves as opposed to the opacity of the metals.

8. If we assume, in accordance with what has been stated, that the various spectra to which I have referred are really due to different molecular aggregations, we shall have the following series, going from the more simple to the more complex:—

First stage of complexity of molecule .....	} Line-spectrum.
Second stage .....	
Third stage .....	} Channelled space-spectrum. Continuous absorption at the blue end not reaching to the less refran- gible end. (This absorption may break up into channelled spaces.)
Fourth stage .....	
Fifth stage .....	} Continuous absorption at the red end not reaching to the more refran- gible end. (This absorption may break up into channelled spaces.)
	Unique continuous absorption.

9. I shall content myself in the present note by giving one or two instances of the passage of spectra from one stage to another, beginning at the fifth stage.

From 5 to 4.

1. The absorption of the vapours of K in the red-hot tube, described in another note, is at first continuous. As the action of the heat is continued, this continuous spectrum breaks in the middle; one part of it retreats to the blue, the other to the red.



From 4 to 3.

1. Faraday's researches on gold-leaf best illustrate this; but I hold that my explanation of them by masses of two degrees of complexity only is sufficient without his conclusion ('Researches in Chemistry,' p. 417), that they exist "of intermediate sizes or proportions."

From 3 to 2.

1. Sulphur-vapour first gives a continuous spectrum at the blue end; on heating, this breaks up into a channelled space-spectrum.

2. The new spectra of K and Na (more particularly referred to in the third note) make their appearance after the continuous absorption in the blue and red vanishes.

From 2 to 1.

1. In many metalloids the spectra, without the jar, are channelled; on throwing the jar into the circuit the line-spectrum is produced, while the cooler exterior vapour gives a channelled absorption-spectrum.

2. The new spectra of K and Na change into the line-spectrum (with thick lines which thin subsequently) as the heat is continued.

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GEOLOGICAL SOCIETY.

[Continued from p. 153.]

March 25th, 1874.—John Evans, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "On the Upper Coal-Formation of Eastern Nova Scotia and Prince Edward Island, in its relation to the Permian." By Principal Dawson, LL.D., F.R.S., F.G.S.

The author described the Carboniferous district of Pictou County as showing the whole thickness of the Carboniferous system arranged in three synclinals, the easternmost consisting of the Lower series up to the Middle Coal-formation, and including all the known workable Coal-measures in the district,—the second towards the west of the middle and the lower part of the Upper Coal-formation,—and the third showing in its centre the newest beds of the latter. On the north the bounding anticlinal of the first depression brings up the New-Glasgow Conglomerate, which contains boulders 3 feet in diameter, often belonging to Lower Carboniferous rocks, and represents the upper part of the Millstone-grit or the lower part of the Middle Coal-formation. The author regards this as representing an immense bar or beach, which protected the swamps in which the Pictou main coal was formed.

The succession of the deposits above the Conglomerate was described in some detail as seen in natural sections. The Upper Coal-formation, as shown in the section west of Carribou Harbour, consists of:—1. Red and grey shales and grey, red, and brown sandstones; and 2. Shales, generally of a deep red colour, alternating

with grey, red, and brown sandstones, the red beds becoming more prevalent in the upper part of the section. In Prince-Edward Island beds apparently corresponding to these are found, and also gradually become more red in ascending. These are overlain, apparently conformably, by the Trias.

The author gave a tabular list of 47 species of plants found in the Upper Coal-formation of Nova Scotia and Prince-Edward Island, and stated that all but about ten of these occur also in the Middle Coal-formation. The number of species decreases rapidly towards the upper part of the formation; and this is especially the case in Prince-Edward Island, some of the beds in which are considered by the author to be newer than any of those in Nova Scotia. The plants contained in the upper deposits were compared with those of the European Permian, and a correlation was shown to exist between them; so that it becomes a question whether this series was not synchronous with the lower part of the Permian of Europe, although in this district there is no stratigraphical break to establish a boundary between Carboniferous and Permian. The author therefore proposes to name these beds Permo-Carboniferous, and regards them as to some extent bridging over the gap which in Eastern America separates the Carboniferous from the Trias.

2. "Note on the Carboniferous Conglomerates of the eastern part of the Basin of the Eden." By J. G. Goodchild, Esq. Communicated, by permission of the Director-General of the Geological Survey of the United Kingdom, by H. W. Bristow, Esq., F.R.S., F.G.S.

The author commenced by describing in detail the series of beds between the true Basement series of the Carboniferous and the Mountain Limestone as shown in sections at Ash Fell. The general sequence in descending order is as follows :—

- a. Carboniferous Limestone, with a few thin beds of stained sandstone and shale; thickness not less than 1000 feet;
- b. Obliquely laminated soft red sandstones, with coal-measure plants, frequently conglomeratic, alternating with fossiliferous shales and beds of limestone; thickness about 500 feet;
- c. Limestone, 500 or 600 feet thick, passing down into
- d. Shales with thin impure limestones, passing down through calcareous conglomeratic beds into a series of apple-green quartz conglomerates and chocolate and grey shales, succeeded without any clear line of separation by the drift-like red conglomerates, sandstones, and shales forming the lower part of the Carboniferous Basement beds, which has been regarded as the equivalent of the Upper Old Red elsewhere.

The author described the mode of occurrence of these deposits in various parts of the district under consideration, and the disturbances which have affected their surface distribution. Along the Cross-Fell escarpment a group of sandstones and conglomerates occupies an exceedingly prominent position, especially at and near

Roman Fell, whence the author proposes to call these deposits the Roman-Fell beds. These beds represent the series *b*, and also the lower part of *a*, at Ash Fell. Following their outcrop towards Cumberland, the conglomeratic beds from the middle downwards increase much in thickness and become much coarser. The author regards the Roman-Fell beds as approximately on the horizon of the Calceiferous Sandstone series of the south of Scotland; and he remarks that they are locally undistinguishable from much of the Basement series, and have been described by authors as undoubted Old Red Sandstone.

3. "An Account of a Well-section in the Chalk at the North end of Driffield, East Yorkshire." By R. Mortimer, Esq. Communicated by W. Whitaker, Esq., F.G.S.

In this paper, which was in continuation of a former communication to the Society (Q. J. G. S. vol. xxix. p. 417), the author stated that the well-section referred to passed through 7 feet of clay and 47 feet of chalk, the upper 3 or 4 feet of the latter very rubbly and broken. The chalk was bedded in laminæ of from  $\frac{1}{16}$  in. to 16 in. thick. From a depth of 20 feet downwards the well exposed many nearly vertical partings running in all directions through the Chalk; and the surfaces of the blocks thus marked out showed numerous striæ, such as were described in the author's former paper. These striæ were in most cases horizontal; but some surfaces showed them at an angle of 45° to the horizon. The laminæ of which the chalk was composed were separated by layers of a softer substance like fuller's earth, containing 1·67 per cent. of organic matter, 7·05 per cent. of oxide of iron, 10·23 per cent. of alumina, and 34·80 per cent. of silica. The author regards this soft substance as formed by the disintegration of chalk, shells, &c., caused probably by the periodical prevalence of great waves or other disturbances in the Cretaceous sea. The effect of its formation he considers would be to check the upward growth of the mass of chalk, which he now, as formerly, ascribes to the direct secreting action of numerous zoophytes. In support of this view he states that the surfaces of the chalk laminæ are more or less irregular—and not even, as if produced by quiet sedimentary deposition. The paper contained detailed analyses of the chalk and of the soft partings.

4. "On Slickensides or Rock-striations, particularly those of the Chalk." By Dr. Ogier Ward. Communicated by Prof. Morris, F.G.S.

The author referred to previous communications on this subject, and maintained that the striæ observed in chalk are to be regarded as slickensides caused by disturbance and movement of the rock. He described the appearances in detail, and mentioned the occurrence of similar striations in various rocks.

April 15th, 1874.—John Evans, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "About Polar Glaciation." By J. F. Campbell, Esq., F.G.S.  
The author commenced by referring to a reported statement of

Prof. Agassiz, to the effect that he supposed the northern hemisphere to have been covered in glacial times from the pole to the equator by a solid cap of ice. He described his observations made during 33 years, and especially those of last summer, when he travelled from England past the North Cape to Archangel, and thence by land to the Caucasus, Crimea, Greece, and the South of Europe. His principal results were as follows:—In advancing southwards through Russia a range of low drift hills occurs about  $60^{\circ}$  N. lat., which may perhaps form part of a circular terminal moraine left by a retreating polar ice-cap; large grooved and polished stones of northern origin reach  $55^{\circ}$  N. lat. at Nijni Novgorod, but further east and south no such stones could be seen. The highest drift beds along the whole course of the Volga seem to have been arranged by water moving southwards. In America northern boulders are lost about  $39^{\circ}$ , in Germany about  $55^{\circ}$ , and in Eastern Russia about  $56^{\circ}$  N. lat., where the trains end and fine gravel and sand cover the solid rocks. Ice-action, in the form either of glaciers or of icebergs, is necessary to account for the transport of large stones over the plains, and the action of moving water to account for drift carried further south. There are no indications of a continuous solid ice-cap flowing southward over plains in Europe and America to, or nearly to, the Equator; but a great deal was to be found on shore to prove ancient ocean circulation of equatorial and polar currents, like those which now move in the Atlantic, and much to prove the former existence of very large local ice-systems in places where no glaciers now exist.

2. "Note regarding the occurrence of Jade in the Karakash Valley, on the southern borders of Turkestan." By Dr. Ferdinand Stoliczka, F.G.S., Naturalist attached to the Yarkund Mission.

In this paper the author described the jade-mines on the right bank of the Karakash river formerly worked by the Chinese. There are about 120 holes in the side of the hill; and these at a little distance look like pigeon-holes. The rocks are a thin-bedded rather sandy syenitic gneiss, mica- and hornblende-schists, traversed by veins of a white mineral, apparently zeolitic, which in turn are traversed by veins of jade.

April 29, 1874.—John Evans, Esq., F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Gault of Folkestone." By F. G. H. Price, Esq., F.G.S.

The author divided the Gault into two great sections, Upper and Lower Gault, which he again subdivided into eleven well-defined zones, mostly named after characteristic Ammonites. Each of these zones or beds is numbered, commencing with No. XI., the zone of *Ammonites interruptus*, which bed forms the base of the Gault, reposing upon the Folkestone beds of the Upper Neocomian.

He found the thickness of the deposit at Copt Point to be 99 feet 4 inches.

He had collected as many as 228 species from the beds, including the following new species—*Avellana pulchella*, *Natica obliqua*, and *Nucula De Rancei*—which he described.

The paper was accompanied by a table of species, setting forth the various beds in which the particular fossils have been met with.

2. "On the Cretaceous Rocks of Beer Head and the adjacent Cliff-sections; and on the relative Horizons therein of the Warminster and Blackdown Fossiliferous deposits." By C. J. A. Meyer, Esq., F.G.S.

The author remarked that in advancing westward from the Isle of Wight the Cretaceous rocks diminish steadily, although unequally, in thickness, and change slightly both in mineral character and fossil contents, while the base of the series rises gradually in the cliff-sections. The chalk-cliffs of Beer Head, the most westerly chalk promontory in England, owe their preservation, in his opinion, partly to a local synclinal arrangement of the strata. The Cretaceous rocks of the district include the following, in descending order:—

Upper Chalk (in part)?  
Middle Chalk.  
Lower Chalk.  
Chalk Marl.  
Chloritic Marl.  
Upper Greensand.  
Gault.  
(?)

The author described in detail the minor subdivisions of these series, and gave lists of the fossils found in them *in situ*. The base of the section is occupied by beds which he identified with those of Blackdown, certainly underlying the Upper Greensand, and apparently occupying the position of the Gault or of the Gault and Upper Neocomian in part. The Warminster beds, on the contrary, were said to cap the Upper Greensand, and to be in reality Chloritic Marl. The author suggested that the term Upper Greensand should be applied exclusively to beds between the Gault and Chloritic Marl, and that the latter should be considered a distinct division.

May 13th, 1874.—John Evans Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "Note on some of the Generic Modifications of the Plesiosaurian Pectoral Girdle." By Harry G. Seeley, Esq., F.L.S., F.G.S.

The author stated that Plesiosauria differ from all living reptilia, except Chelonians, in wanting a sternum, and pointed out the resemblance between the plesiosaurian coracoid and the coracoid and precoracoid of Chelonians, inferring that the plesiosaurian scapulæ had been carried forward by the potential ossification which elon-

*Phil. Mag.* S. 4. Vol. 49. No. 324. March 1875. R

gated the plesiosaurian neck. He compared the chelonian plastron with the plesiosaurian girdle-bones, to show the dependence of form in the chelonian type upon the potential energy due to the conditions of locomotive activity, and used this consideration in elucidation of chelonian and plesiosaurian resemblances and differences. The plesiosaurian interclavicle he regarded as homologous with the chelonian and lacertian interclavicle; but the chelonian clavicles he believed to be epiphysial, potential representatives of the precoracoids, and therefore bones of which no analogues should be sought in Plesiosaurs on the theory of their chelonian affinities. He believed that the clavicles were occasionally distinct from the interclavicle, though usually blended with it, just as all these ossifications become obliterated by scapular extension.

The restorations and interpretations of the plesiosaurian pectoral girdle given by Conybeare, Hawkins, Owen, Huxley, Cope, and Phillips were discussed, and reasons given for dissenting from their views. The old genus *Plesiosaurus* was divided into two families—the Plesiosauridæ, containing the genus *Plesiosaurus*, and the Elasmosauridæ, with *Eretmosaurus*, *Colymbosaurus*, and *Murænosaurus*.

A new type was taken for the genus *Plesiosaurus*, which showed distinct clavicles. *Eretmosaurus* has neither clavicle nor interclavicle; and the scapulæ, concave in front, are blended in the median line, and blended laterally with the coracoids. Its type is *Plesiosaurus rugosus* of the Lias. *Colymbosaurus* has for its type *Plesiosaurus megadeirus* of the Kimmeridge Clay. It has no interclavicle; the scapulæ are prolonged forward in a wedge, and backward so as to meet the coracoids in the median line and enclose two coraco-scapular foramina.

*Murænosaurus* is founded on a new type from the Oxford Clay. It has no interclavicle; but the scapulæ are prolonged forward to meet in the median line; they are not prolonged backward to meet the coracoids; hence but one coraco-scapular foramen is formed. A similar condition marks the pelvic girdle.

2. "*Murænosaurus Leedsii* (Seeley), a Plesiosaurian from the Oxford Clay."—Part I. By Harry G. Seeley, Esq., F.L.S., F.G.S.

All parts of the animal, except teeth, ribs, and hind limbs, were described. The premaxillary bones extend bird-like between the nares to the frontals. The foramen parietale is between the parietal and frontal, and directed backward. The cerebral lobes of the brain have a chelonian form, are prolonged in olfactory nerves, like those of *Teleosaurus*, and have the optic lobes moderately developed. The exoccipital bones do not enter into the occipital condyle. The basisphenoid is perforated by the carotids, as in *Ichthyosaurus*. The hypoglossal nerve does not perforate the exoccipital bone.

There are 44 cervical, 3 pectoral, 20 dorsal, 4 sacral, and the first 8 caudal vertebræ preserved. Atlas and axis are ankylosed. The zygapophyses are semicylindrical, being concave in front and convex behind. A process of the neural spine is prolonged between the anterior zygapophyses, so as to divide the posterior zygapo-

physes and lock between them. The caudal vertebræ have the facets for the chevron bones free from the articular margins, forming large prominent unequal tubercles on the base of the centrum. The coracoids are as broad as long, nearly square, not prolonged in front of the humeral articulation. The scapulæ are sickle-shaped, thin towards the median line, and without any suprahumeral process. The pubic bones are transversely oblong, and the ischial bones more than usually triangular, owing to there being no forward prolongation to meet the pubes. The iliac bones are less expanded at the proximal end, and relatively longer than usual. In the limbs the ulna and radius approximate in form to those bones in *Pliosaurus*, and the phalanges resemble those of *Pliosaurus* in not being compressed from side to side. There are six polygonal carpal bones.

3. "On the remains of *Labyrinthodonta* from the Keuper Sandstone of Warwick, preserved in the Warwick Museum." By L. C. Miall, Esq. Communicated by Prof. Huxley, F.R.S., F.G.S.

In this paper the author first noticed the remains of *Labyrinthodonts* from the Warwickshire Keuper, acquired by the Warwick Museum since 1842, the date of Prof. Owen's memoir on this subject, and then reviewed the determinations of Prof. Owen. He considered that *Labyrinthodon ventricosus*, Owen, is not a distinct species, and that *L. scutulatus*, Owen, has not been proved to be a *Labyrinthodont*. The species as identified by the author are as follows :—

*Mastodonsaurus Jægeri*, Von Meyer.

— *pachygnathus*, Owen.

*Labyrinthodon leptognathus*, Owen.

*Diadetoagnathus* (g. n.) *varvicensis*, sp. n.

In conclusion the author described some of the structural peculiarities of the teeth of various *Labyrinthodonts*.

## XXVIII. Intelligence and Miscellaneous Articles.

### ON MAGNETISM. BY A. TRÈVE.

IF we place between the poles of the large electromagnet of Ruhmkorff the two extremities of the thick wire into which the current passes from the pile—in other terms, if the circuit be closed between the two poles, we get neither spark nor report; but when we open it a violent detonation is produced, "almost as powerful as the report of a pistol," says M. A. de la Rive, who first made the discovery. The learned Genevan physicist adds, "it seems that the intensity of the extra current is greatly augmented in this case by the influence of the poles of the magnet." This is the phenomenon which I have essayed to fathom.

Is it necessary to interrupt the current between the two poles in order to obtain this effect? No. If we increase the distance

between the two poles of the electromagnets in order to study only their isolated action, we shall quickly verify:—

- (1) That the phenomenon announced by De la Rive is equally produced within the sphere of attraction of either of those poles;
- (2) That the phenomenon is not inherent in the inducing current alone, but that the current from any independent pile, interrupted within that sphere of attraction, gives rise to the same effects.
- (3) That the extra current receives a very real and considerable augmentation of tension.

Oxygen being magnetic (as M. Edm. Becquerel has proved), there was room to ask if some action of condensation or separation of the constituent elements of air did not take place in the magnetic field of the pole. I therefore collected, by means of ordinary aspirators, air from several points in that field; and analysis of it revealed none of these peculiar actions.

To give still more precision to this research, M. Duboseq and I investigated the interference-phenomena, by submitting one of the two luminous rays, or both at once, to the action of a powerful electromagnet. The apparatus employed was the interferential reflector of M. Jamin. We caused the two rays, or one of them, to pass successively into air, oxygen, nitrogen, hydrogen, carbonic acid; and in each of these different cases we could never observe the slightest displacement of the fringes.

The hypothesis of an atmosphere of *vibrating æther* around the poles of magnets (a conclusion to which I have thought I could come) would perhaps permit us to understand a little better than it has yet been comprehended the phenomenon of induction by magnets, discovered by Faraday.

I seize this opportunity to say that I have repeated the experiment of induction *in vacuo*, and at all pressures, without ascertaining the least alteration, either to more or less, in the intensity of the current produced.

To this communication the author adds a Note relative to "the magnetic atmosphere of magnets." From some experiments, which are to be realized with greater precision by means of apparatus which is now being constructed, he believes he can infer the mode of action of an electromagnet upon a cylinder of soft iron placed along its axis.—*Comptes Rendus de l'Acad. des Sciences*, vol. lxxx. pp. 310–311.

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ON A NEW ELECTROMAGNET, FORMED OF CONCENTRIC TUBES OF IRON SEPARATED BY LAYERS OF CONDUCTING WIRE. BY J. CAMACHO.

The new electromagnet, of which I have the honour to forward a sketch to the Academy, was constructed for the purpose of obtaining very considerable dynamic effects with relatively feeble currents.

Each of the cores consists of a series of concentric tubes, the intervals between them being nearly equal to their thickness; on



each of the tubes an insulated wire of copper is wound, always in the same direction, the thickness of the layer of wire being greater on the outermost tube. The extremities of the wire belonging to each tube traverse the breech and are united so as to form only one single conductor arranged in the following manner: the wire, after being wound round one of the two outside tubes, passes on to the inner tube next to this, then upon the tube concentric to the preceding, and so on to the central tube of this core; then, having run along the breech, it is wound round the central tube of the second core, within which core it follows a course the reverse of that indicated for the first core; that is to say, after winding round each of the concentric tubes successively and in the same direction, passing from the smallest to the largest, it issues finally after enveloping the outside tube of the second core\*.

The following is the result of some experiments made with this electromagnet:—

Employing the current of ten Bunsen elements of the usual size with bichromate of potass, the attractive force of the electromagnet at a distance of  $12\frac{1}{2}$  millims. is 713 kilogrammes, and the time required for the development of the magnetism to raise this weight is 1.33 second.

If we cut the wires which pass from one core to the other, then connect the four free ends crosswise (that is, connect the lower end of the wire of the right core with the upper end of the wire of the left core, and the upper end of the wire of the right core with the lower end of that of the left core), and then pass the current of the same ten elements, but combined in two parallel series of five elements each, the power of the electromagnet is unchanged, but the time necessary for the magnetization is reduced to one fourth, or to 0.33 second.

If, finally, each of the two coils of the electromagnet be covered with a round shield of soft iron, thus binding the upper part of the four concentric cores which constitute it, the electromagnet loses some of its power, and is reduced to the condition of an ordinary electromagnet with a solid core.

After indicating the theoretical considerations which led to the arrangement adopted, the author continues:—

“Experiment has shown that, if we cover the polar extremities of the tubes constituting each core with a round shield of iron, the electromagnet loses its great power and is again in the same condition as an ordinary electromagnet. In fact, the magnetism received by the shields will have been developed by the influence of

\* The diameter of the outside tube is  $12\frac{1}{2}$  centims., and the thickness of the concentric tubes, which are four in number, is about 6 millims.; the insulated copper wire is 1.8 millim. in diameter; and the number of helices of wound wire is seven to the outermost, and only two between each of the series of concentric tubes forming a core. In these conditions, the height of the cores being 20 centims., the total length of the wire is about 600 mètres; its weight, corresponding to this length, is 11.5 kilogrammes; and the total number of turns is 2000.

the polar extremities of all the tubes in contact with them : but these polar extremities cannot develop a magnetism greater than that which they possess, and that only on those atoms of the shields with which they are in contact ; so that the magnetism of the atoms situated on the other side of the shields (that is, at the outside) will be very feeble, in consequence even of the thickness of the latter.

“ Moreover, as the free extremities of the tubes of which each core consists have each of them the same magnetic pole, on uniting them to one another by a round shield of iron, between these poles reactions are developed which diminish the magnetic force of the system, just as happens in bundles formed of permanent magnets.”—*Comptes Rendus de l'Académie des Sciences*, Feb. 8, 1875, vol. lxxx. pp. 382–384.

ON THE EXPERIMENTAL DETERMINATION OF DIAMAGNETISM BY ITS ELECTRICAL INDUCTIVE ACTION. BY PROF. A. TOEPLER, OF GRATZ.

As is well known, Faraday and Weber have shown that diamagnetic bodies, when brought nearer to or moved further from a closed spiral in a powerful magnetic field, generate induction-currents. These certainly very feeble currents produced by the motion of the diamagnet have even been made use of by Weber in order, by means of a very sensitive apparatus, to compare the polarity of bismuth with that of iron.

The electrical-induction currents, however, can be observed and measured without moving the diamagnet, by means of the diamagnetism which is produced and vanishes—whereby the process is in many respects simplified. I use for this purpose a differential inductor with a system of commutators, in the following manner:—

Let two spirals (A and B) of thick wire be inserted one behind the other in the circuit of a series of constant intensity, and two induction-spirals (*a* and *b*) nearly identical in constitution placed in their cavities. Let the latter be likewise one behind the other, but closed at opposite ends by a galvanometer. At the opening and closing of the principal circuit the galvanometer is acted on by only the difference of the two inductions ; and this difference is quite eliminated by adding to the more feebly acting induction-spiral (for instance, *b*) a small auxiliary spiral, which is inserted with it in the galvanometer-circuit, and shifted by a micrometer-screw towards the principal spiral B until the galvanometric effect of the closing and opening vanishes even with a principal current of great intensity. If now a magnetic or diamagnetic body be placed in the middle of the other coil (*a*), the galvanometer again gives, on the closing and opening of the principal circuit, the induction of the moment which is produced and vanishes.

But this method (which, besides, was in like manner recommended by Dove for feebly magnetic bodies such as nickel &c.) is quite in-

adequate for the purpose of ascertaining extremely feeble induction-currents through diamagnetic substances. For this I combine with it a process of multiplication similar to Weber's, but with three commutators.

A commutator (I.) alternates in very rapid succession the direction of the current in A and B. A second commutator (II.), moved by the same mechanism, turns the conduction of the spirals *a* and *b* to the galvanometer in such wise that all the induction-actions of the diamagnet which arise in *a* on the alternation of the principal current, arrive in the same direction at the galvanometer. These induction-shocks (10–12 per second) give, according to known laws, a constant displacement from the position of rest. This enduring deflection can be directly observed. In harmony with all the investigations hitherto made, it appears that the arising and vanishing diamagnetism induces in neighbouring conductors currents *opposite in direction* to those obtained by means of magnetic bodies.

Observation becomes still more convenient and sensitive when another, a special commutator (III.) is brought into the galvanometer-conduction, which the observer, after the known method of multiplication, turns at the end of each oscillation until the amplitude reaches its extreme value. Of course small deviations from perfect compensation of the coils *a* and *b* must be determined by comparing observations with and without a diamagnet, and taken into account. In this way, with proportionally small spirals (A and B 500 turns each; *a*, *b*, and galvanometer each 1000), I obtained, the galvanometer being moderately astatized, a constant extreme amplitude of 15 scale-divisions by means of six Bunsen cells and inside the induction-spiral a bundle of rods of bismuth of 200 grms. weight; while a particle of fine iron wire weighing only 0.0044 gm. gave 556 scale-divisions in the opposite direction. With very delicate astatizing a single Bunsen cell was sufficient, with the above means, for the perception of the induction-current by the diamagnetism of the bismuth.

In this place I recommend also for similar observations a very simple modification of the mirror-galvanometer, by which four times instead of twice the angle of deflection is measured. Opposite to the galvanometer-mirror a fixed horizontal strip of looking-glass is placed, at a distance from 10 to 15 centims., and the telescope and scale adjusted so that the rays of light meet the galvanometer-mirror twice before entering the telescope—which is easily accomplished if the dimensions of the mirror are suitable. From the reading *s* the deflection-angle  $\alpha$  is found according to the formula

$$\tan \alpha = \frac{s}{4(D+d)},$$

in which *D* and *d* denote the distances of the scale and the fixed auxiliary mirror from the mirror of the galvanometer. This

arrangement is recommended in those cases where the measurement of the angle cannot be carried to a greater nicety by increasing the magnifying-power of the telescope or by large scale-distances.

In the above-described process for observing diamagnetism, beside the slight action to be measured, an incomparably greater one, the direct induction of the spirals, must be compensated. It is therefore a principal thing with the apparatus to be able to ensure the compensation and preserve it unaltered. This is only possible when the system of commutators (I. and II.) satisfies certain conditions in its construction, to be more particularly described in another place, and when the spirals are well insulated, so that in their windings no secondary closings variable with the temperature shall exist. Now these conditions, as we learn from observation, can be fulfilled with very remarkable completeness; and hence, in my institute, diamagnetic measurements will be carried out according to this method with more powerful spirals.

I have also executed another (and, so far as I know, undescribed) form of differential inductor, with which the induction produced by the arising and vanishing magnetism upon the principal current is observed. Let four branches A, B, C, D be, after the manner of Wheatstone's combination, united so that the principal current divides into two branches  $A+B$  and  $C+D$ , and let the bridge together with the galvanometer be inserted between the angle-points A B and C D. Let the branches A and C contain each a single spiral of great magnetizing force. Now let the action of the stationary current upon the galvanometer be compensated by resistances in B and D. The action, in general still present, of the extra currents at the closing and opening of the circuit is compensated separately, by micrometrically displacing fine iron rodlets in the less powerful spiral until the galvanometer shows neither stationary nor momentary deflections. Induction, however, is immediately again produced by the opening and closing when a feebly magnetic body is placed in the other spiral; this can, as before, be multiplied and measured.

It is true that this last method is far more difficult in practice; but it might be suitable for the investigation of certain reactions on current-electricity. Thus, for example, by it one might study the question whether the rotation of the polarization of light in magnetic or diamagnetic bodies under the influence of the current reacts on the current, which, with present views on electricity and the luminiferous æther, is not improbable. It was intended observations of this kind that induced me to make the above-described preliminary experiments on electrical induction-currents through diamagnetic bodies.—*Kaiserliche Akademie der Wissenschaften in Wien, Sitzung der math.-nat. Classe, January 21, 1875.*

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XXIX. *On the Comparison of some Tube and other Spectra with the Spectrum of the Aurora.* By J. RAND CAPRON, Esq., F.G.S.\*

[With Four Plates.]

IN a contribution by the late Professor Ångström to the solution of the problem of the aurora-spectrum (an abstract of which appears in 'Nature' of the 16th July, 1874), the Professor is stated, amongst other things, to have laid down certain propositions in substance as follows:—

1st. That the aurora has *two* different spectra—the one comprising the one bright line in the yellow-green only, and the other the remaining fainter lines.

2ndly. That the bright line falls within a group of hydrocarbon lines, but does not actually coincide with any prominent line of such group, and that Herr Vogel's finding this line to coincide with a not well-marked band in the air-spectrum must be regarded as a case of accidental coincidence.

3rdly. That moisture in the region of the aurora must be regarded as *nil*, and that oxygen and hydrogen<sub>o</sub> must alone there act as conductors of electricity. Professor Ångström then details the examination of an exhausted dry air-flask filled with a discharge analogous to the glow of the negative pole of a vacuum air-tube, and, comparing this with the aurora-spectrum, gives the following results:—

Aurora-lines, wave-lengths	4286	4703	5226
Violet light, „	4272	4707	5227

Two weak light bands found by Herr Vogel at 4663 and 4629

\* Communicated by the Author.

are also compared with other lines in the violet light 4654 and 4601; and the Professor then concludes that it may be in general assumed *that the feeble bands of the aurora-spectrum belong to the spectrum of the negative pole, possibly changed more or less by additions from the banded or the line air-spectrum.*

4thly. That the only probable explanation of the *bright line* is that it owes its origin to *fluorescence* or *phosphorescence*, the Professor remarking on this point that "an electric discharge may easily be imagined which, though in itself of feeble light, may be rich in ultra-violet light, and therefore in a condition to cause a sufficiently strong fluorescence," remarking also that oxygen and some of its compounds are fluorescent.

5thly. That there is no need, in order to account for the spectrum of the aurora, to have recourse to the "very great variability of gas-spectra according to the varying circumstances of pressure and temperature" (Dr. Vogel's theory). Professor Ångström does not admit such variability, and does not admit that the way a gas may be brought to glow or burn can alter the nature of the spectrum.

In order to test the Professor's conclusions in an experimental way, I have recently examined some tube and other spectra not only for line-positions, but also for general resemblance to an aurora-spectrum. These experiments, few at first, led to others; and the results, though not perhaps developing any striking or new features, may help to clear the way on some points, and to suggest further experiments bearing on an interesting subject, which up to the present time has been almost entirely in the hands of foreign spectroscopists. It did not seem desirable to use powerful currents: a  $\frac{1}{2}$ -inch-spark coil worked by a quart bichromate-cell was found sufficient to illuminate the tubes steadily. The spectroscope used was one made for me by Mr. Browning specially for auroral purposes; of the direct-vision form, with five large prisms, the collimator and telescope having clear 1-inch lenses.

The field of view extends at one glance from near C to near G, the extremities of the spectrum being obtained by traversing with the telescope; with a fine slit the D line is widely separated. In the eyepiece is inserted a reduced scale (photographed on microscopic glass and mounted in balsam) of bright lines or spaces upon an opaque ground. The faintest spectrum brought in part upon this scale shines through the spaces and renders the divisions visible, showing the spectrum-lines above and touching them. The drawings were made on enlarged photocopies of the microscopic scale itself, so as to avoid any chance of error as between the actual scale and the copy used for the drawings. I found this plan the most effective for rapid and correct sketching; and it gives close results as compared with

other recognized micrometer-measured spectra when they are compared. In most cases the central part of the spectrum only (corresponding to the central lines of the aurora) is mapped, the red line in the aurora not being found to correspond with any prominent line in the gas-spectra examined, and the auroral line near solar G being at present so indefinitely fixed as to render comparison almost valueless. I have selected Dr. Vogel's spectrum as given in his Memoir ('English Mechanic,' vol. xviii. No. 461, p. 446) for comparison, it being, so far as I am aware, the most accurately mapped with regard to wave-length at one observation of any auroral spectrum, and it seeming an unsafe plan to attempt to obtain an average aurora by comparison of differing observations made at various times by different observers with all sorts of instruments—the difficulty, too, being increased by the suspicion that the spectrum itself at times varies in number and position, as well as intensity of its lines.

In illustration of the difficulty of constructing any thing like a general typical aurora-spectrum I append a Table of eight auroral spectra taken at hazard.

### Aurora Lines and Bands.

Observers.      Red.   Yellow.   Green.   Blue.   Indigo.   Violet.

Vogel, April 9, 1871 .....	6297	5569	5390	5233	5189	5004	{ 4694 to 4629 }	...
Barker, Nov. 9, 1871 .....	6230	5620	...	...	5170	5020	4820	...
Barker, Oct. 14, 1872 .....	6300	5550	{ 5330 to 5200 }	5320	{ 5050 to 4990 }	4930	4740	4310
A. Clarke, jun., Oct. 24, 1870	...	5690	...	...	...	...	4850	4350
Backhouse, 1873 .....	6060	5660	...	...	5165	5015	...	4305
Backhouse, Feb. 4, 1874.....	*	5570	..	...	5180	4980	4830	4320
H. R. Procter, 1870.....	*	*	...	*	...	...	*	*
Lord Lindsay, 1870.....	...	*	*	*	*	...	...	*

\* Mr. Procter's and Lord Lindsay's lines had no wave-lengths given to them. No doubt some of the discrepancies are instrumental and personal; but there is, I think, still enough remaining of discrepancy to lead to the inference that the aurora prevails in distinct forms or types, and with the fainter lines or bands differing in position. From notes and drawings kindly supplied at times to me by Mr. Backhouse, there is also no doubt that the relative intensity of the lines frequently differs. With a sufficient number of observations these forms or types might be systematically arranged and compared, with a prospect of advancing our knowledge of the nature of auroræ.

I shall feel much indebted to any observers who will furnish me, for this particular purpose, with charts of spectra and wave-lengths of lines: these last, however, I can, more or less perfectly, deduce from such drawings, if the positions of a few solar or other well-known lines are marked on the scale.

Dr. Vogel's spectrum does not comprise the line near G; but I have added this (in an approximate place only) in order to complete the set of lines. For drawing of Dr. Vogel's spectrum, with its scales attached, see Plate III.

### *Hydrogen-Tube.*

This tube was one of Geissler's and of rather small calibre. On illumination the wide ends were easily lighted with a silver-grey glow, having a considerable amount of stratification. The capillary part glowed brilliantly with silver-white, bright green, and crimson light according to the intensity of the current; with the commutator slowly working, white running into green and bright green were the main features of the thread of light; on the current passing more rapidly the capillary thread became of an intense crimson, at the same time apparently increasing in diameter, an effect probably due to irradiation.

The spectrum was very brilliant, consisting of the three bright lines usually distinguished as  $H\alpha$ ,  $H\beta$ , and  $H\gamma$ , and a number of shaded bands and fainter lines between these, with a bright continuous spectrum as a background to the whole.

The lines  $H\alpha$ ,  $H\beta$ , and  $H\gamma$  were found to vary in intensity with the current, and in accordance with the colour of the light as seen by the eye—a fact, as I think, not without bearing on the question of the aurora, the varying tints of which are so well known. The fainter lines or bands were mostly stripes of pretty equal intensity throughout, and all about the width of the  $H\beta$  line. I did not trace any marked degrading on either side of the lines, though the edges were not uniformly so sharp as  $H\alpha$  and  $H\beta$ ; some of the lines are coincident in position with lines of the air-spectrum.

One line only actually coincides with the aurora-spectrum, this being that to which Dr. Vogel assigns an identical wave-length, viz. 5189. Other lines, however, fall somewhat near the aurora-lines 5569, 5390, 5233, and 5004, two faint lines also falling within the band 4694 to 4629.

The lines (adopting Dr. Vogel's wave-lengths for the H lines) are, when compared, as under:—

Aurora .	5569	5390	5233	5189	5004	$\left\{ \begin{array}{l} 4694 \\ \text{to} \\ 4629 \\ 4632 \end{array} \right.$
Hydrogen	5555	5422	..	5189	5008	

I remarked that a line 5596, described by Dr. Vogel as "very bright" in his H spectrum, does not appear in my tube, though in most other respects our H spectra agree.

I thought this tube afforded a good opportunity for testing the



effect of distance upon the spectrum. The slit was made rather fine. At 6 inches distance from it the line *a* (see drawing) in the blue-green (F solar) was very bright. The lines marked  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , and  $\zeta$  also survived, but were faint. At 12 inches from the slit *a* and  $\gamma$  were alone seen; and at 24 inches *a* stood by itself upon a dark ground. I also noticed that the red and yellow parts of the spectrum first lost their light on the tube being withdrawn from the slit; and this appeared to account for  $\beta$  disappearing while  $\gamma$  survived. For drawing of the hydrogen-spectrum see Plate IV. spectrum 1.

*Carbon and Oxygen Tubes.*

By way of introduction let me state that I do not here propose to enter into the question now vexed by Professor Piazzi Smyth as to the real character of the carbon-spectrum, and that when I speak of carbon-tubes and spectra I use the words in a general sense, and as meaning those tubes and spectra which have hitherto passed under that designation.

The following tube-observations have been taken together, because my friend, Mr. Henry R. Procter (to whom I am in debt for many profitable hints and suggestions in auroral work) is disposed to regard the spectra found in the carbon-tubes, and in those marked "O," as identical; considering that pure O with the ordinary non-intensified discharge gives only a continuous spectrum, and that the O tubes are in fact generally lighted up by a carbon-spectrum, the result of impurity from accidental causes. The tubes examined for the purpose of comparison were as follows:—A coal-gas tube, a tube marked "C.A.," three O tubes, two of (I believe) London make, and the third from Geissler, and an  $\text{OH}_2$  tube, also from Geissler. The carbon-tubes were both brilliantly and steadily lighted by the current. The C.A. tube glowed with a peculiar silvery grey green light in the capillary part, and with a grey glow considerably stratified in the bulbs. The coal-gas-tube discharge was whiter and still more brilliant than the C.A., and with even finer stratification in the bulbs. The spectra of both tubes were conspicuous for the same three well-known principal bright lines or bands in the yellow, green, and blue (with one fainter in the violet), all shading off towards the violet, and in both cases with fainter intervening bands or lines; and these last bands or lines only partially coincided when the two tubes were compared.

The spectra in both cases were rich and glowing, with a certain amount of continuous spectrum between the lines; and the three principal bands or lines in both cases showed well and distinctly their respective place-colours.

*Tested for distance.*—In the case of the C.A. tube at 18 inches from the slit the continuous spectrum and fainter lines disappeared, while the four principal lines still shone out, that in the green being the strongest. At 24 inches the same lines were still visible, though somewhat faintly.

In the case of coal-gas, at 24 inches the whole spectrum was quite brilliant, the four principal lines being very bright, and even preserving their distinctive colours. The H line, near the line or band in the blue, was also plainly seen. The O tubes, when treated by the same current as the carbon-tubes, were found to be all three identical in general features. The discharge lighted up each of the tubes feebly and somewhat intermittently. Grey in the bulbs, and a faint but decidedly pinkish white in the capillary part, were the distinguishing light colours, while nothing could be more marked than the difference in brilliancy between these and the preceding carbon-tubes.

The  $\text{OH}_2$  tube presented very much the same character; but the discharge occasionally varied from a pinkish white to a yellow colour, somewhat like what artists call brown pink, reminding one of the "golden rays" in certain auroræ. These O spectra presented, in common with the carbon-tubes, three principal bright lines or bands in the yellow, green, and blue, with a fainter one in the violet, all shading off towards the violet. The bands, however, showed but very little trace of local colour; and the whole spectrum had a faint and washed-out look, very different from the carbon-spectra. (I certainly by a little management subsequently succeeded in getting the same look to the C.A. spectrum; but it was only by removing the tube to some distance from the slit, and thus depriving the spectrum of very much of its brightness.) The hydrogen line (solar F) was bright, more so than any of the O lines. The intensity of the three principal lines seemed to me to run in the following order:—

	Yellow.	Green.	Blue.
Coal-gas . . . . .	$\beta$	$a$	$\gamma$
Oxygen . . . . .	$\gamma$	$a$	$\beta$

Between the lines  $\gamma$  and  $a$  in the Geissler O tube I found a rather bright line, which I shall have occasion to refer to hereafter.

At 12 inches distance from the slit the O spectrum lost nearly all its light; the H line and the three lines  $\gamma$ ,  $a$ , and  $\beta$  alone faintly remaining,  $a$  being decidedly the brightest. At 24 inches no spectrum at all was to be seen.

I carefully compared together the three principal lines of the two spectra of coal-gas and O by means of:—

1st, the photographed micrometer before described;

2nd, a comparison-prism on the slit plate;

3rd, a piece of very fine brass foil cut as a pointer and fixed in the focus of a positive eyepiece.

The lines or bands in both tubes were found to be slightly nebulous towards the less-refrangible end (where they were measured), and the O tube was not bright under a moderately high power (positive eyepiece); but, subject to these remarks, *the three principal lines in both tubes were found to correspond in position within the limits of my instrument.* The spectra did not, however, I am bound to say, *look alike.*

I was naturally puzzled by these observations; and it then occurred to me to reduce Dr. Vogel's spectrum of O, given in his memoir, to the same scale with my own. This I did independently; and I then compared the result with my own spectrum as mapped out; and from it I judge that if my O tubes, one and all, showed a carbon-spectrum, the learned Doctor's tube must have been subject to a similar infirmity, as the tubes all agree in main features.

There is, however, one point to which I desire to draw attention, which is this, that common to both the Doctor's and my own Geissler spectrum I find the before-mentioned rather bright line between  $\gamma$  and  $\alpha$ . This line I find no equivalent for in either of the carbon-tubes. For spectra of coal-gas and oxygen see Plate IV. spectra 2, 3 & 4.

In comparing the spectra, the reader should remember that the tube- and flame-spectra of carbon do not correspond. Compare, for instance, the spectrum of coal-gas or C.A. in tube and the well-known lines or bands in the blue base of a candle-flame. The sharper edge of the yellow line or band of the carbon-tubes will be found about midway between the two bright yellow candle-lines or bands. The first of the very beautiful group of lines or bands in the green in the candle-flame falls considerably behind the sharper edge of the green line or band in the tube, while the third bright band in the tube alone of the three corresponds with a very faint band in the candle-flame, and a line or band in the violet in the tube-spectrum finds no equivalent in the candle-spectrum. For comparison of the carbon-tube and flame-spectra (the principal lines of the tube being alone given) see Plate VI. spectra 6 & 7.

From Dr. Watts's 'Index of Spectra' I have extracted the three principal carbon-tube bands or lines; and they compare with Dr. Vogel's oxygen-tube as under:—

	Yellow.	Green.	Blue.
Dr. Vogel's oxygen-lines	5603	5195	4834
Dr. Watts's carbon-tube	5622	5189	4829
bands or lines . }			

The 5622 for the yellow line of the tube must be an error. 5608 seems to me, from my own observations, nearer its place; and I calculate 5193 and 4825 for the other lines; so that the two spectra (if I am correct) would compare thus:—

Oxygen . . . .	5603	5195	4834
Carbon . . . .	5608	5193	4825

Now these wave-length differences are so small that they raise a presumption of the possibility of the spectra being identical; but, on the other hand, assuming the spectra are not identical, the comparison tells the other way, viz. that the differences are so far minute as to escape detection in instruments of moderate dispersion; and with my own instrument I found the O spectrum too faint to increase the dispersive power with advantage. Considering the extremely different character of the two discharges, the identity of all the O tubes, and the presence of the line found between  $\gamma$  and  $\alpha$  in the O spectrum, I think the two spectra are independent, though I admit there is room for doubt.

I ought to mention that the tube O H<sub>2</sub> gave the principal lines of the O and H spectra combined, on a faint continuous spectrum.

I next examined two vacuum-tubes of an entirely different character. The one was a tube from Geissler of stout glass, some 15 inches long, without electrodes, and an inch across. Within this tube is a second of uranium glass with bulbs blown in it; and in contact with both tubes a quantity of fluid mercury runs loose. Upon shaking this tube with the hand, brilliant flashes of blue white light like summer lightning flash out. These are discernible (though faintly) even in daylight.

The fine terminal wires of the coil being wrapped round each end of this tube, when the current passed a bright and white induced discharge, with a considerable amount of stratification, was seen in the tube.

The other tube was that of an old mercurial siphon barometer. This being placed in a stand, one terminal wire was placed in the mercury in the short leg of the siphon, while the other terminal was made into a little coil and placed on the upper closed extremity of the barometer-tube. On passing the current the entire short space above the mercury was filled with a grey white light, not stratified, but showing a conspicuous bright ring just above the level of the mercury.

Both these tubes, when examined with the spectroscope, showed four bright rather uniform bands (the central one being the brightest), which I assign to the carbon-spectrum (see Plate IV. spectra 5 & 6).

The Geissler tube was probably filled designedly with coal-gas. In the case of the barometer-tube, the spectrum may be assumed to be the result of some carbon impurity.

No lines of mercury could be detected in either case.

*Air-Tubes.*

As the air-spark spectrum may be said in some form to represent lightning, so it would seem not unreasonable to expect a rarefied-air spectrum to represent the aurora; and indeed it has long been the practice in lecture-rooms to exhibit with considerable success exhausted air-tubes excited by electricity as "aurora" tubes. The first tube I examined was an ordinary Geissler tube charged with rarefied air. The bulbs, on passing the discharge, were filled with the well-known rose-tinged light, like to the aurora-streams, which in the capillary part was condensed into a brighter and whiter thread, while the platinum wire of the negative pole was surrounded by its usual mauve or violet glow.

The spectrum, even with a weak current, was quite bright, and consisted mainly of the nitrogen-lines and bands, with the lines  $H\alpha$ ,  $H\beta$ , and  $H\gamma$ , and some of the intermediate lines of the H spectrum.

The double line  $\alpha$  was undoubtedly the brightest in the spectrum when taken in the capillary part of the tube. After this followed  $\beta$ , and then  $\gamma$  (H),  $\delta$ , and  $\epsilon$ ; but I am uncertain as to the relative brightness of the three, and mark their intensities with hesitation. I tested them several times independently with differing results, and I suspect them of variability with the current.

The rest of the lines are very much of the same intensity. (For drawing of spectrum of air-tube in capillary part see Plate V. spectrum 1.)

I next turned my attention to the violet or negative-pole glow; and here a remarkable change takes place in the spectrum, not only in the position of the principal bands or lines, but in their relative intensity (see Plate V. spectrum 2).

The double line  $\alpha$  in the capillary part is replaced in the violet glow by a shaded band of second intensity  $\beta$ , the sharp edge of which is extended towards the red and forms (except for some faint indications) the limit of the spectrum in that direction. The somewhat faint line next  $\alpha$  in the capillary tube has its faint representative in the violet-pole; but the next two lines (capillary) are represented by the bright band  $\gamma$  in the violet-pole lying in a position between them. Next  $\gamma$  in the violet-pole come three faint lines representing  $\beta$ ,  $\gamma$ , and  $\delta$  in the capillary spectrum; and then comes the bright band  $\alpha$ , which

is the brightest of the violet-pole group, and which represents a medium-intensity band in the capillary spectrum. After this is a faint band near  $\alpha$ , representing two rather bright ones in the capillary spectrum, this last being succeeded by other bands in the violet.  $\alpha$ ,  $\beta$ , and  $\gamma$  in the violet-pole were examined carefully for relative brightness, and are, I believe, correctly marked.

The red- or positive pole was next examined, but presented no peculiar features. It appeared as a fainter representation of the capillary air-spectrum with some few lines or bands absent; and, as will be seen after, it is also a fair representation of a diffused air-spectrum (see Plate V. spectrum 3).

Examined for comparative intensity, at 24 inches from the slit, the whole capillary air-spectrum showed faintly—the marked lines in the centre of the spectrum generally retaining their prominence; but after  $\alpha$  I judged  $\epsilon$  next in brightness. On examining the violet pole at 12 inches from the slit, the whole spectrum was faint, and the bands  $\alpha$  and  $\beta$  were alone distinctly seen.

Next to the Geissler air-tube I examined an “aurora”-tube, about 15 inches long and  $1\frac{1}{4}$  inch across, with platinum terminals and of the same diameter throughout. The discharge was of a rosy red colour; and the long flickering stream from pole to pole certainly much reminded me optically of an auroral streamer. Spectroscopically examined, the discharge presented a faint banded air-spectrum similar to that of the positive pole (see Plate V. spectrum 4); but the relative intensity of the lines was somewhat altered, while a very bright line in the green (seen also in the tube next described) was characteristic of the spectrum, and in this respect distinguished it from the ordinary air-spectrum.

Following this last tube I examined one purchased as “phosphorescent.” It was rather short ( $6\frac{1}{2}$  inches), of equal calibre, and about the size of the bulb of a Geissler tube. It was filled with a white powder (probably one of the Becquerel compounds). On passing the current between the electrodes a bright rose-coloured stream appeared; and wherever this was in contact with the powder, the tube glowed with a brilliant green light. On stopping the current the tube still continued to shine, but with a fainter green glow, which gave only a continuous spectrum. When examined in full glow, the tube-spectrum was also in the main continuous and of a green tinge; but upon it were lines or bands in the blue and violet portions of the spectrum (which I have not yet worked out), while in the red, yellow, and green a faint but distinct air-spectrum was seen; and with this was also found the same bright line in the green which distinguished the “aurora”-tube.

I next took a  $\frac{1}{2}$ -inch spark in air between platinum terminals

(see Plate V. spectrum 6). The principal lines in this spectrum were the line  $\alpha$  (by far the brightest) corresponding to  $\gamma$  in the violet pole; next was  $\beta$ , a line in the yellow not appearing in the tube-spectrum, and then other lines of less intensity. In the "aurora"- and "phosphorescent" tubes was found, as before mentioned, a line prominent for its brightness, and, indeed, in the "aurora"-tube the only one which survived when it was moved away from the slit. This line also appears in the spark-spectrum, but there only of an average brightness. I examined it carefully for position in the respective tubes, and on comparing them found it coincident with the ridge or centre of the wedge-like bright green broad band which is so conspicuous in the air-tube spectrum.

I think this edge-like centre has actually a line coincident with the line I refer to; but if so, its intensity little exceeds that of the band itself.

To complete the set of air-experiments, I examined the same spark taken from the surface of a small meniscus of water placed upon the lower platinum wire. In this case the air-spectrum was plainly, but not brightly, seen at the violet end of the spectrum; the red, yellow, green and blue being filled with a continuous spectrum through which some of the air-lines faintly showed (see Plate V. spectrum 7). I reserve the remarks on the position of the air-lines as compared with those of the aurora till later.

#### *Phosphoretted-Hydrogen Flame.*

This was obtained from an ordinary hydrogen-bottle fitted with glass tubing, two or three minute pieces of phosphorus being placed with the zinc. The flame was of a bright yellow colour with a vivid cone of green light in its centre.

The spectrum was found to consist mainly of three bright bands in the yellow, green, and green-blue respectively (see Plate VI. spectrum 1).

The centre band was very striking in its emerald-green colour, while all the bands were remarkable as being very broad in proportion to the slit (which, however, was not fine). The yellow band had also a rich glow of colour. My spectrum was mapped out at ordinary temperature, and I found the bands sufficiently bright; but Mons. Lecoq de Boisbaudran, in his '*Spectres lumineux*' (Texte, p. 188), has described how the brilliancy of these bands is increased when the flame is artificially cooled (*refroidie*). He also makes the important remark that the relative intensities of the bands are in such case altered, adding:—"La plus importante de ces modifications consiste en un ren-

forcement très-considérable de la bande rouge  $\delta$  97.03 (W. L. 5994) qui devient vive de presque invisible qu'elle était en l'absence du refroidissement artificiel de la flamme." May not this explain the varying intensity of the red line (and perhaps the green also) in the aurora?

### *Iron-Spectrum.*

A comparison of this spectrum suggested itself to me (as it has previously done to others), partly from the suspected relations between the aurora and the corona, and partly from a consideration of the views lately expressed by M. Gronemann and others in favour of the aurora having its origin in the fall of an incandescent meteoric powder.

The spectrum was obtained from a spark taken over a solution of perchloride of iron, and was remarkable for its brightness in and about the green region. The lines varied considerably in intensity; and with a fine slit the principal ones were sharp, distinct, and clear. A group of three lines (*a*) stood out boldly in the green as the most marked, and next to these a group of three others more towards the violet end of the spectrum (see Plate VI. spectrum 4). By the side of my own phosphoretted-hydrogen and iron spectra I have placed the principal lines as given in Mons. Lecoq de Boisbaudran's same spectra (reduced of course to my scale), and with figures of wave-lengths for comparison with the aurora-spectrum; and to these comparisons I shall refer hereafter (see Plate VI. spectra 1 & 2).

### *Spectrum of Mercury.*

This spectrum is only given as useful for comparing with the bright and principal aurora-line. It is easy to obtain with a small coil, the metal being used as one electrode. The yellow lines are distinct and steady; but the green, which is very bright, is apt to flicker as the spark moves on the surface of the metal (see Plate VI. spectrum 5).



TABLE showing comparative position of Aurora-lines with principal lines in the examined spectra. C means coincident within the limits of my instrument and scale, N near, and V N very near.

Aurora lines .....	6297 β	5569 α	5390 ζ	5233 δ	5189 δ	5004 γ	4694 to 4629 ε	4350 ? ε
Hydrogen-tube.....	No results in the examined spectra, but see Plate III. fig. 2.	N	...	N	C same W. L.	...	Band includes 2 lines.	Too uncertain in position for comparison (see Plate III. fig. 1).
Coal-gas tube .....		...	...	N	V N	...	Band includes 1 line.	
Oxygen-tube.....		...	...	...	V N	...	...	
Air, capillary .....		Band includes	Band includes	...	N	...	Band includes 2 lines.	
Air, violet-pole.....		...	...	...	Band includes	C	Band includes 1 line.	
Air, red-pole.....		See air,	capillary.					
Aurora-tube and phospho- rescent tube .....		See air,	capillary; and		note	bright	line.	
Air, spark .....		N	...	...	N	C	Band includes 2 lines.	
Air, spark, over water .....		Continu	ous spect	rum and	faint air	-lines.	Band includes 2 lines.	
Phosphorescent hydrogen...		N	Faint band	Band includes	...	...	...	
Iron .....		V N	N	V N	V N	...	...	

### Conclusions.

I intended to conclude the preceding observations with a few remarks on Professor Ångström's propositions, for the purpose of discussing how far the latter seemed in accord with the above experiments. My attention, however, has been called to an extract from a letter written by Professor A. S. Herschel to R. H. Scott, Esq., and printed in the Philosophical Magazine for January 1875, in which Professor Ångström's memoir is also reviewed and discussed.

I propose to have this letter in view while drawing some conclusions from my own observations; and in the outset I candidly confess I hesitate to indorse Professor's Herschel's axiom, that Professor Ångström's memoir is "conclusive and satisfactory," and that "little more will be done now by future observers than to verify his conclusions and extend their researches in the direction he points out."

Of course no memoir on the aurora from so high an authority as the late Professor Ångström can be aught than highly interesting and instructive; and I quite appreciate that the Professor has opened up new and apt discussion (especially upon the subject of the presumed phosphorescent or fluorescent character of the bright aurora-line); but, on the other hand, I find reason to differ from him in his absolute conclusions as to the violet-pole spectrum; and on some other points in his memoir, I further feel strongly that whatever advance the learned Professor's memoir may have made in that direction, there is still plenty of auroral ground left for spectroscopists to work upon, and that the legacy Professor Herschel speaks of, though undeniably rich, may, like some other legacies, give rise to a good deal of discussion among the legatees before its benefits are reached.

Professor Ångström's principal propositions seem to be these:—

1st. Two auroral spectra. I agree in this, but question whether the fainter lines may not comprise more than one spectrum.

2nd. I agree also that the bright yellow-green line falls, as Professor Ångström describes, just behind the second line in the hydrocarbon yellow group. And I find, in common with the Professor, no well-marked or prominent line in the air-spectrum with which it accords.

3rd. This may be conveniently divided into two parts, viz.:—

A. The proposition that "moisture in the region of the aurora must be regarded as *nil*."

Here I see reason to differ, since (to quote a letter of Mr. Procter's) "the vapour-density of  $\text{OH}_2$  is only 9 against 14 for N and 16 for O;" and again, "electrical or heat-repulsion (*vide* Crookes and Faye) may carry water-dust up to enormous heights." There are, too, I think, circumstances connected with the aurora itself which make the fact of moisture being *nil* in the auroral regions quite unlikely. The first of these is the fact that the white arc, streamers, and floating patches of light found in some auroræ have frequently the peculiar dense and solid look of vapour clouds—a circumstance with which I have been frequently struck. Mr. Procter also suspects that the aurora is generally formed in a sort of "mist or imperfect vapour." The second, that auroræ, or portions of them, are, as I believe, frequently close to the earth's surface (for instances see 'English Mechanic,' vol. xviii., No. 460, p. 419). The arc of a fine white aurora which I saw at Kyle Akin (Skye) last autumn had quite a solid and misty look, while one of its extremities had the appearance of being behind a near range of mountains, but in

front of a more remote range. On this point, too, note the peculiarities of the red line, which (and, as I find, the green line also) is coincident with, or very close to, telluric bands or groups of lines in the solar spectrum (see Plate III. fig. 2).

I think we may also claim the continuous spectrum in the aurora in further proof of water-vapour (see Plate V. spectrum 7). The continuous spectrum of the aurora is also to my eye more local and dense in the spectroscope than the usual spectrum seen between the lines or bands in gases.

B. The question of the violet-pole spectrum. And here I start with the remark that, in comparing other spectra with the aurora, it is, I think, too much the practice to trust to the coincidence (more or less perfect) of one, or perhaps two lines out of many, whereas we know by experience that most spectra have so well-marked a general as well as special character, that when once seen they are recognized afterwards with the greatest ease and without measurements. Of course no two given spectra could be considered identical unless their principal lines coincided; but, on the other hand, the coincidence of one or two lines out of many without other features cannot be satisfactorily or conclusively held to establish identity.

In Professor Herschel's letter (Phil. Mag. No. 322, p. 71)

Professor Ångström's representation of the "spectrum of the glow discharge round the negative pole of air-vacuum tubes" is given, in comparison with the aurora-lines and those of olefiant gas.

I presume, from an examination of the spectra in this woodcut, that those of the violet-pole and of olefiant gas have been accidentally transposed. Assuming this to be so, yet the scale is too small to work satisfactorily with, and I must fall back upon my own spectrum-plates to found my remarks upon. I should also state that (assuming the mistake above mentioned) Professor Ångström's projection and my own of the violet-pole spectrum, still differ in some respects, though otherwise they have a common resemblance. This will be seen on reducing them to the same scale.

As the general result of my observations and drawings, *I see no reason for giving to the violet-pole glow any special or distinguished place in comparison with the aurora*, far less for assigning to it the nearly absolute monopoly of the spectrum. It is true that the line  $\gamma$  in the violet-pole glow is in close coincidence with one of the aurora-lines; but how are the brighter bands  $\alpha$  and  $\beta$  accounted for? These, as I have before pointed out, alone survive when the tube is placed at a distance; and it is true they are thus reduced to shaded-off lines; but the difficulty still remains, that they are conspicuous for their absence in the aurora-spectrum; and I cannot but think, on the whole, that if the violet-

pole spectrum is to represent the aurora-spectrum, it must be under very different conditions from those under which it obtains in air-vacuum tubes.

4th. I feel much more in accord with Professor Ångström's memoir upon the subject of the phosphorescence or fluorescence of the bright yellow-green aurora line.

I do not notice that the Professor touches upon the external features of the aurora in respect of these phenomena; perhaps the following extracts from my own note-book on this point may not be uninteresting. I quote from them as made at the time.

October 20th, 1870.—I noted the grand auroral display of that evening including "streamers of *opaque white phosphorescent cloud* very different from the more common transparent auroral diverging streams of light." (On this occasion, too, I may mention I saw sharp and clear both the red and the green lines with Browning's miniature spectroscope. I also noted a peculiar flickering of the green line.)

February 4th, 1872.—A fine display. The first signs were (in dull daylight) "a lurid tinge upon the clouds, which suggested the reflection of a distant fire, while, scattered among these, torn and broken masses of *white vapour having a phosphorescent appearance*" . . . . . reminded me of a similar appearance in October 1870. Then follows a description of the formation of the corona. Day auroræ too, not unfrequently recorded, we should suppose could hardly be seen without the presence of some phosphorescent glow.

Having regard to the near proximity of the phosphoretted-hydrogen band to the bright aurora-line, to the circumstance of this band *brightening by reduction of temperature* (a phenomenon probably connected with ozone), to the peculiar brightening of one line in the "aurora" and "phosphorescent" tubes, and to the observed circumstance that the electric discharge has a phosphorescent or fluorescent afterglow (I believe this was isolated by Faraday), I feel there is strong evidence in favour of such an origin to the principal aurora-line, *if not to the red line as well.*

5th. Professor Ångström opens a wide door to discussion in his proposition of the invariability of gas-spectra; and I cannot now attempt to follow this interesting part of the present subject. Suffice it to say that, if the Professor makes this assertion in its strictest sense (I can hardly suppose he so means it), there is, so far as I am aware, no one spectrum that can claim place with the aurora-spectrum. Giving greater latitude to the Professor's words, we may I think assume upon competent authority that lines vary in *number and brilliancy* with *temperature*, and in *breadth* with *pressure*; and again, Kirchhoff, in speaking of vapour films as increasing the intensity of lines, states "*it may happen*

*that the spectrum appears to be totally changed when the mass of vapour is altered."* I suppose, too, we may now add *magnetism* as capable of effecting a change in certain spectra—though this subject is at present new and only partially explored.

Thus far I have given the results of some observations made with a view to test experimentally Professor Ångström's conclusions on the aurora-spectrum. It will no doubt be remarked by some who look at my drawings, that I have obtained a number of negatives, but that there is no positive result anywhere. I quite admit this, and am disappointed in so doing; but then it must be remembered that one way of finding out what a thing is, is to find out what it is not. I venture to think, however, we may not consider the time entirely thrown away, and that, although no one examined spectrum complies with all the auroral conditions, we may still usefully examine the set in regard to their relative proximity thereto.

Tested by coincidence or close proximity of lines to those of the aurora we may arrange the spectra in the following order:—1, iron; 2, air-spark; 3, hydrogen; 4, air-tube spectrum; 5, phosphoretted hydrogen; 6, carbon and oxygen.

The air-tube spectrum might perhaps stand higher in the scale but for its broad bands, which make comparison doubtful. Lines of oxygen possibly escape detection in the aurora from the faint character of its spectrum.

The phosphorus and iron spectra are specially interesting in connexion with Professor Nordenskiöld's "metallic and magnetic cosmic dust in the polar regions" (see *Phil. Mag.* vol. xlviii. No. 321, page 546).

If asked to give an opinion in the present state of our knowledge of the aurora question, I should say:—

1st. That the yellow-green line, and possibly also the red, are due to phosphorescence or fluorescence. 2nd. That the fainter lines are partly due to the air-spectrum (but not specially the violet-pole), in which H lines probably play a prominent part, and the spark-spectrum appears nearer the mark than the tube-spectrum; and that the remaining bands or lines may be due to phosphorus and iron (the close coincidences in this latter spectrum with the aurora-lines being certainly very striking). All these spectra seem to me to claim special and further attention; and to them I would add that of  $\text{OH}_2$  in relation to auroræ of a dense and misty character.

For measuring auroral and other lines, a cheap and very effective micrometer is constructed by making the whole slit-plate of the spectroscope (and consequently the spectrum itself) traverse the field with a fine micrometer-screw, a pointer or pointers being fixed in the eyepiece. My early observations were made with

one of Browning's larger direct-vision spectroscopes fitted in this way. Large aperture, however, both of prisms and lenses, is almost indispensable in observations of faint auroral spectra. I close this by adding a few remarks to Professor Herschel's list of auroral lines (appended to his letter), which may be useful to other observers.

*Remarks by way of addition to Professor Herschel's list of auroral lines\*.*

1. *Red line*.—On my scale coincident with telluric group *a* in solar spectrum. I found at the same time a faint telluric band or group coincident with the yellow-green line.

2. *Yellow- or citron-green line*.—I always see this more pale green than yellow; sometimes flickering and changing in intensity (Professor Herschel has also noted this on one occasion). Not always sharp. Procter has recorded it nebulous; might not its appearance in regard to width, intensity, and sharpness be made a test of height of the aurora?

3. *Greenish-blue or blue lines*.—One cannot help suspecting difference of position as well as of intensity of lines in the central portions of auroræ. We know how varying auroræ are in general character and appearance; and although no doubt much must be allowed for hasty observation, often made with imperfect instruments so far as measuring is concerned, there still seems a residuum of considerable difference in the position of lines to be accounted for. Lines Nos. 1 and 2 are closely fixed; but I would counsel special attention to the places of the fainter lines; and it might be useful to put No. 2 out of the field, or hide it by a bar while observing these.

*Indigo and violet lines, Nos. 5 and 6*.—As mentioned before, No. 5 seems most indefinitely positioned; No 6 I have never been fortunate enough to see.

XXX. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

II.

[Concluded from p. 218.]

*Chlorides of the Alkaline Earths.*

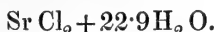
§ 78. **CHLORIDE** of Barium.—The chloride of barium in saturated solution becomes a solid cryohydrate at  $-8^{\circ}$  C. Of the portion last to solidify, 6.6790 grms. gave, on evaporation and heating to  $350^{\circ}$  C., 1.5490 Ba Cl<sub>2</sub>. This corresponds to 23.2 per cent. Of a previous crop of crystals, 6.1350

\* See also 'English Mechanic,' January 16th, 1874, No. 460.

grms. gave 1.4735 Ba Cl<sub>2</sub>, or 24.0 per cent. The first of these shows the formula

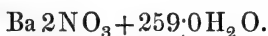


§ 79. *Chloride of Strontium*.—This salt forms a cryohydrate at  $-17^\circ$ . Of the final portion, 5.8325 grms. contained 1.6085 of SrCl<sub>2</sub>, or 27.57 per cent. The crop before this showed 1.3655 grm. of salt in 4.9675 solution, or 27.5 of Sr Cl<sub>2</sub>. We may therefore deduce the formula

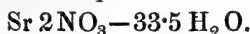


#### *Nitrates of the Alkaline Earths.*

§ 80. *Nitrate of Barium*.—The cryohydrate of this salt solidifies from a saturated solution at  $-0.8^\circ$ . I have only one determination of its composition; namely, 3.0370 grms. gave 0.1610 of anhydrous salt, which corresponds to 5.30 per cent., and the molecular ratio

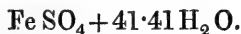


§ 81. *Nitrate of Strontium*.—On cooling a saturated solution to  $-6^\circ$  the cryohydrate solidifies. Of the last portion, 6.8010 grms. gave 1.7675, or 25.99 per cent. of Sr2NO<sub>3</sub>. Of the previous crop of the cryohydrate, 4.6715 grms. contained 1.2105 of the anhydrous salt, or 25.91 per cent. These determinations concur towards the relationship



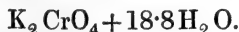
#### *Miscellaneous Cryohydrates.*

§ 82. *Sulphate of Iron*.—Green vitriol separates from a saturated solution at  $-2.2^\circ$ . The next to the last portion of the cryohydrate showed the following composition:—4.7000 grms. gave 0.8155 FeSO<sub>4</sub>, or 17.35 per cent. Of the last portion, 4.8140 grms. gave 0.8155, corresponding to 16.94 per cent., and showing the ratio



Although the solution of this salt was quite clear when hermetically sealed for analysis in a tube containing not more than .5 cubic centim. of air, a considerable deposit of sesquioxide took place. The analysis, therefore, is probably not quite exact.

§ 83. *Chromate of Potassium*.—The cryohydrate solidifies at  $-11^\circ$ . Of the last crop of crystals, 3.0690 grms. gave 1.1145 anhydrous salt, or 36.27 per cent. Of a previous crop, 5.4775 grms. gave 1.9945, or 36.41 per cent. The first indicates the formula

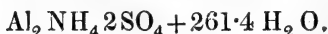


From § 28 the bichromate has a cryohydrate solid at  $-1^\circ$  and

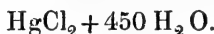
containing 292 molecules of water. Accordingly

	Temperature of solidification.	Water-worth.
Chromate, $K_2CrO_4$	. $-11^{\circ}$	18.8
Bichromate, $K_2Cr_2O_7$	. $-1$	292.0

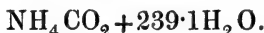
§ 84. *Ammonium Alum.*—This body was examined on account of the large percentage of water which is held by the ordinary hydrated salt. The cryohydrate solidifies at  $-0^{\circ}.2$ . The part last to solidify was examined; of this, 4.3845 grms. contained 0.2060 gm. of anhydrous alum. This shows 4.7 per cent. Of the immediately preceding crop of crystals, 5.2400 grms. gave 0.2220 of anhydrous alum, or 4.2 per cent. The first of these determinations indicates the relationship



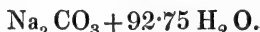
§ 85. *Perchloride of Mercury.*—A saturated solution of corrosive sublimate solidifies at  $-0^{\circ}.2$ . The ultimate and penultimate portions were examined. Of the former, 6.0640 grms. gave 0.197, or 3.24 per cent.; of the latter, 4.977 grms. gave 0.164, or 3.29 per cent. The first indicates the formula



§ 86. *Oxalate of Ammonium.*—This solidifies as a cryohydrate at  $-0^{\circ}.2$ . Of the last portion to solidify, 4.340 grms. contained 0.125, or 2.8 per cent. of the anhydrous salt. This agrees with the relation



§ 87. *Carbonate of Sodium.*—After igniting the carbonate so as to decompose any bicarbonate, the saturated salt solidifies as a cryohydrate at  $-2^{\circ}$ . Of the final portion, 6.4090 grms. contained 0.383 of  $Na_2CO_3$ . This shows 5.97 per cent., or the relation



§ 88. The following Table shows at a glance the relation between the lowest attainable temperature when the salt is mixed with ice, the temperature of the solidification of the cryohydrate, the water-worth or aquavalent. Column 1 shows the salt employed, and the degree of hydration when associated with water of crystallization. Column 2 shows the temperature obtained when the salt is mixed with ice. Column 3 shows the temperature at which the cryohydrate separates. In column 4 are shown the number of molecules of water associated with one molecule of the salt in the cryohydrate. It is here called "water-worth." In column 5 are the percentages of the anhydrous salt which the final portions of the cryohydrates contained,



according to the analyses given above. The letters M.L. show that the liquids here analyzed stood before solidification in the relationship of mother-liquors to the preceding crops of cryohydrate. In column 6 are analyses of the crop of cryohydrate immediately preceding the last cryohydrate. The salts are arranged according to the degree of cold attainable when the salt is used as a cryogen, *i. e.* in a freezing-mixture.

TABLE X.—Showing (1) the chemical formula of the salt, (2) the lowest temperature to be got by mixing the salt with ice, (3) temperature of solidification of the cryohydrate, (4) molecular ratio between anhydrous salt and water of its cryohydrate (water-worth or aquavalent), (5) percentage of anhydrous salt in portion of cryohydrate last to solidify, (6) percentage of anhydrous salt in crop of cryohydrate before the last.

(1) Formula of salt.	(2) Temperature of cryogen.	(3) Temperature of solidification of cryohydrate.	(4) Molecular ratio or water-worth or aquavalent.	(5) Percentage of anhydrous salt in last cryohydrate. M.L.	(6) Percentage of anhydrous salt in next to last cryohydrate.
NaBr .....	-28°	-24°	8·1	41·33	41·61
NH <sub>4</sub> I .....	-27	-27·5	6·4	55·49	57·6
NaI .....	-26·5	-15	5·8	59·45	59·39
KI .....	-22	-22	8·5	52·07	51·72
NaCl .....	-22	-22	10·5	23·60	
SrCl <sub>2</sub> + 6H <sub>2</sub> O .....	-18	-17	22·9	27·57	27·5
NH <sub>4</sub> SO <sub>4</sub> .....	-17·5	-17	10·2	41·70	42·2
NH <sub>4</sub> Br .....	-17	-17	11·1	32·12	32·17
NH <sub>4</sub> NO <sub>3</sub> .....	-17	-17·2	5·72	43·71	43·26
NaNO <sub>3</sub> .....	-16·5	-17·5	8·13	40·80	41·3
NH <sub>4</sub> Cl .....	-16	-15	12·4	19·27	19·27
KBr .....	-13	-13	13·94	32·15	31·80
KCl .....	-10·5	-11·4	16·61	20·03	20·07
K <sub>2</sub> CrO <sub>4</sub> .....	-10·2	-12	18·8	36·27	36·41
BaCl <sub>2</sub> + 2H <sub>2</sub> O .....	-7·2	-8	37·8	23·2	24·0
Sr <sub>2</sub> NO <sub>3</sub> .....	-6	-6	33·5	25·99	25·91
MgSO <sub>4</sub> + 7H <sub>2</sub> O .....	-5·3	-5	23·8	21·86	
ZnSO <sub>4</sub> + 7H <sub>2</sub> O .....	-5	-7	20·0	30·84	
KNO <sub>3</sub> .....	-3	-2·6	44·6	11·20	
Na <sub>2</sub> CO <sub>3</sub> .....	-2·2	-2	92·75	5·97	
CuSO <sub>4</sub> + 5H <sub>2</sub> O .....	-2	-2	43·7	16·89	
FeSO <sub>4</sub> + 7H <sub>2</sub> O .....	-1·7	-2·2	41·41	16·92	17·35
K <sub>2</sub> SO <sub>4</sub> .....	-1·5	-1·2	114·2	7·80	7·5
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .....	-1	-1	292·0	5·30	
Ba <sub>2</sub> NO <sub>3</sub> .....	-0·9	-0·8	259·0	5·30	
Na <sub>2</sub> SO <sub>4</sub> + 10H <sub>2</sub> O .....	-0·7	-0·7	165·6	4·55	
KClO <sub>3</sub> .....	-0·7	-0·5	222·0	2·93	2·88
Al <sub>2</sub> NH <sub>4</sub> 2SO <sub>4</sub> + 12H <sub>2</sub> O .....	-0·4	-0·2	261·4	4·7	4·2
HgCl <sub>2</sub> .....	-0·2	-0·2	450·0	3·24	3·29

§ 89. *Remarks on Table*—The above Table contains the whole of the salts which I have as yet examined fully. The interesting group of the chlorides of the alkaline earths, including magnesium and the no less interesting group of the perchlorides of aluminium and iron, have presented difficulties with which I am still contending. The same is the case with the nitrate of calcium and the chloride of copper,  $\text{Cu Cl}_2$ .

From the evidence before us I think, however, that I may venture to enunciate the general law, that if we define as similar salts either (1) those which consist of the same acid united with bases belonging to the same chemical group (ex.  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ), or (2) those which consist of the same base united with acids belonging to the same group (ex.  $\text{KNO}_3$ ,  $\text{KClO}_3$ ), or (3) those whose bases belong to the same group, and whose acids belong to the same group—then, *of similar salts, the one which produces the greatest cold when used in a freezing-mixture unites as a cryohydrate with the fewest molecules of water.* And to the following law there seems to be only one pronounced exception: *The temperature at which the cryohydrate is formed is the same as the temperature of the corresponding freezing-mixture.* This latter law, however, has to be taken with reserve as far as those salts are concerned which, like  $\text{AlCl}_3$  and  $\text{MgCl}_2$ , decompose water, and also in regard to those bodies which, like  $\text{CaCl}_2$ , unite with water under the liberation of much heat. These I shall consider in my next communication to the Society.

#### *Cryohydrate of Ethylic Alcohol.*

§ 90. Of very great interest is the behaviour which is shown by mixtures of ethylic alcohol and water when deprived of heat. This interest extends itself in a practical direction, in consequence of the use of alcoholic liquids in regions of extreme cold. We have here at once a new element for consideration. The two liquids are miscible in all proportions. This means that any possible hydrate of alcohol is soluble at ordinary temperatures both in water and in alcohol. I shall use the word alcohol to denote absolute alcohol,  $\text{C}_2\text{H}_6\text{O}$ , and the word "spirit" for a mixture of this with water.

§ 91. The fact so long known, that heat is liberated and volume finally lost when ethylic alcohol is mixed with water, has silently pointed to the conclusion that there must be at least one definite hydrate of alcohol. It is sufficiently clear that if one were forced to the alternative of relying either upon the amount of heat liberated or upon the loss of volume, the former rather than the latter would be the most trustworthy.

§ 92. *Historical.*—A useful historical summary of much of what has been previously done in France in this direction of

research is prefixed to a recent paper on the subject by M. Melsens, in the *Annales de Chimie et de Physique*, entitled "Sur la refroidissement et la congélation des liquides alcooliques et des vins." According to M. Boussingault, frozen wines after thawing furnish an alcoholic liquid and are not therefore pure ice. According to M. Melsens, alcoholic liquids containing about 50 per cent. of alcohol by weight or by volume become at  $-30^{\circ}\text{C}$ . viscid, syrupy, and sometimes opalescent. These represent commercial spirits such as rum, cognac, &c., and may be represented by the formula  $\text{C}_2\text{H}_6\text{O} + 3\text{H}_2\text{O}$ , corresponding to the maximum condensation. According, again, to M. Melsens, when wine which has become semisolid through being exposed to cold of a freezing-mixture is drained through wire gauze or introduced into a turbine, nearly colourless ice free from alcohol is left. From frozen wine containing from 10 to 12 per cent. of alcohol, from 16 to 25 per cent. of pure ice was got by means of a screw press. By the same means a frozen red or white Burgundy yielded 40 per cent. of ice.

§ 93. In the first of a series of able researches on the physical properties of mixtures of water with the alcohols, Messrs. Dupré and Page (Proc. Roy. Soc. March 11, 1869) examined, amongst others, the quantity of heat developed on mixing alcohol and water in various proportions, the specific heat of such mixtures, their capillarity, boiling-point, and their compressibility.

The following fragments of these experimenters' Tables include the critical values.

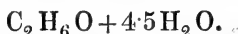
TABLE showing number of heat-units evolved from 5 grammes of mixtures resulting from mixing the percentages by weight of alcohol in column 1 with the complementary percentage of water. The asterisk shows the critical region.

per cent. alcohol.	Heat-units from 5 grms. of mixture.
10 . . . . .	26.68
20 . . . . .	43.95
30 . . . . .	47.98*
40 . . . . .	44.86
45 . . . . .	38.81

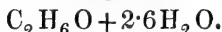
In the next Table Messrs. Dupré and Page's numbers are given, showing the specific heats of such mixtures. The column 1 shows the percentage of alcohol, column 2 the specific heat, column  $\Delta$  the difference between the observed and calculated specific heats.

Alcohol per cent.	Specific heat.	Excess over calculated, $\Delta$ .
10 . . . .	103.58	+ 7.53
20 . . . .	104.36	12.27
30 . . . .	102.60	14.47*
40 . . . .	96.80	12.63
45 . . . .	94.19	12.00
50 . . . .	90.63	10.42

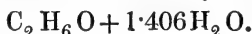
Messrs. Dupré and Page epitomize one branch of their research as follows:—"The whole of the physical characters of mixtures of alcohol and water come to a maximum deviation from their theoretical values somewhere between 30 and 45 per cent. of alcohol by weight. The 30 per cent. nearly corresponds to the formula  $C_2H_6O + 6H_2O$  (29.87 per cent.); the 45 per cent. has approximately the formula  $C_2H_6O + 3H_2O$  (46 per cent.)." The mean of these values is



§ 94. According to Rudberg (Pogg. *Ann.* vol. xiii. p. 496), the contraction is greatest when 55 volumes of alcohol are mixed with 45 volumes of water, or 43.6 weights of alcohol with 45 weights of water. This corresponds to the formula



§ 95. According to Bussy, alcohol not stronger than 33 Beaumé may be frozen by the evaporation of  $SO_2$ . This strength is that of 78.29 per cent. of alcohol by weight, or



According to Marchand (*Journ. für Chemie*, vol. xxv. p. 253), when 1 part by weight of spirit is mixed with 1 part of snow, the depression of temperature depends upon the strength of the spirit, according to the following Table:—

per cent. by weight.	
90 . . . . .	-22
70 . . . . .	-21
60 . . . . .	-19
50 . . . . .	-17.5
40 . . . . .	-16
30 . . . . .	-13
20 . . . . .	- 8

This is, I believe, the condition of the question as left by others.

§ 96. *My own experiments.*—The alcohol I used was shaken with dry carbonate of potassium and distilled from quicklime.

With this I made decimal mixtures ranging from 95 alcohol and 5 of water to 95 water and 5 of alcohol. These were submitted in turn to the action of a cryogen, in order first of all to see at what temperature the solidification of each mixture *begins*. For if, as has been supposed, and quite recently by Melsens again proved, a very weak (10 per cent.) spirit gives up only ice, and since alcohol is notoriously not to be solidified by our most powerful cryogens, it must follow that during the continuous solidification of a weak spirit the temperature must fall continually. Temperatures down to  $-19^{\circ}$  were observed on the mercurial thermometer. For lower temperatures, demanding the employment of solid carbonic acid and ether, use was made of an alcohol thermometer, which was collated with the mercurial one at  $-22^{\circ}$ . The Table gives the temperature at which the solution began to yield solid matter. What this solid matter consists of I have afterwards to consider. Columns  $\Delta_1$  and  $\Delta_2$  are the values of the first and second differences respectively.

TABLE XI.—Temperatures at which Solidification begins in Spirits of various strengths.

Water per cent., by weight.	Alcohol per cent., by weight.	Temperature C. at which solidification begins.	$\Delta_1$ .	$\Delta_2$ .
95	5	$-2^{\circ}$	2.3	+0.6
90	10	$-4.3$	2.9	+0.6
85	15	$-7.2$	3.5	+0.5
80	20	$-10.7$	4.0	+0.7
75	25	$-14.7$	4.7	-0.8
70	30	$-19.4$	3.9	-0.2
65	35	$-23.3$	3.7	+0.3
60	40	$-27$	4.0	+2.0
55	45	$-31$	6.0	-1.0
50	50	$-37$	5.0	-2.0
45	55	$-42$	3.0	+5.0
40	60	$-45$	8.0	?
35	65	$-53$	?	
30	70	$-65$ (not).		

From this Table it is seen that the temperature of initial solidification sinks so regularly that the column of second differences shows for a long time the value 0.6. Only at lower temperatures, which of course cannot pretend to the same degree of accuracy, are serious variations visible. There is a rapid fall at the ratio 35 water to 65 alcohol; and at the ratio 30 water to 70 alcohol, I failed to effect solidification at  $-65^{\circ}$  C.

§ 97. So free from discontinuity are these numbers, that one might be readily misled into the belief that the solid matter

separated is in all cases ice. This, however, is not the case. Down to the ratio 65 water and 35 alcohol, the ice spicula freely moving in the mother-liquid are easily recognized. If they are remelted they invariably reform at the same temperature. At ratios of 60 water to 40 alcohol and stronger, the aspect of the solid formed is quite different. The liquid may then acquire the consistency of Canada balsam, and yet, if kept still, it may remain perfectly transparent. On rubbing with the thermometer-bulb or with a glass rod minute crystals are formed, the liquid becomes more mobile, resembling old honey. It offers a notable case of a condition of supersaturation producing a temporary colloid condition.

§ 98. Finding that this phenomenon was first noticeable at about the solution of the ratio 60 water to 40 alcohol, and reflecting that this is nearly the ratio of one molecule of alcohol to four of water, I made a spirit of exactly this molecular ratio, namely 39.07 alcohol and 60.93 of water by weight. On submitting this to the action of a cryogen, I found the remarkable result that nothing separated till the temperature  $-34^{\circ}$  was reached, although both weaker and stronger solutions begin to solidify at higher temperatures. The solid formed in this case is perfectly white and opaque, and the temperature remains constant till the whole has become perfectly dry. This pearly aspect and the constancy of temperature throughout the solidification betray the cryohydrate. Both weaker and stronger spirits sink in temperature as they solidify—the former until by the elimination of ice it presents a mother-liquor of the 4-hydrate composition, the latter by the elimination of liquid alcohol as the solid 4-hydrate is formed.

§ 99. When, therefore, a dilute alcohol (say 95 water to 5 alcohol) is cooled, ice separates out, the spirit becomes stronger and stronger, and the temperature lower and lower. When the ratio  $C_2H_6O + 4H_2O$  is reached the temperature  $-34^{\circ} C.$  is reached, and the remainder of the solution is a cryohydrate of alcohol whose melting- and freezing-point is  $-34^{\circ}$ , and whose composition is  $C_2H_6O + 4H_2O$ .

On the other hand, if a spirit a little stronger than  $C_2H_6O + 4H_2O$  is subjected to cold, nothing separates till about  $-27^{\circ} C.$  At this temperature the cryohydrate  $C_2H_6O + 4H_2O$  begins to separate out, and as it relinquishes the alcohol the solidifying-point of the mother-liquor falls. Observe, the cryohydrate separates from alcohol at a temperature above its own melting-point when alone. It follows from this that solidification may commence at the same temperature in two spirits of different strengths, provided they are both close about the 4-molecule hydrate in composition. But while in the weaker the solid will be ice, in the stronger it will be the cryohydrate. The apparent anomaly

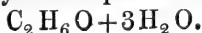
arises from the circumstance that the cryohydrate is soluble both in water and alcohol, and that ice is soluble in the liquid cryohydrate. We are here reminded of the phenomenon of the maximum density of water, which I have already endeavoured to connect with the formation of a cryohydrate of water (in § 36).

§ 100. For some reasons this melted cryohydrate of alcohol, or spirit of wine containing 60·93 water and 39·07 of alcohol, should be the standard or proof spirit in all alcoholometry. English proof spirit contains 50·5 per cent. by weight of alcohol. It accordingly should begin to solidify at  $-38^{\circ}$  (about the freezing-point of mercury). At lower temperatures it becomes a pasty mass, but never perfectly brittle, on account of the unfreezable alcohol in excess above that of the cryohydrate. Spirits of 39 per cent. and under become perfectly solid before the temperature reaches  $-36^{\circ}$ . The very fact that weaker spirits wholly solidify while stronger never do so is, I conceive, a complete proof of the existence of a cryohydrate. For if under all circumstances water alone solidified, alcohol would be left even from the weakest spirits, and total solidity could never be reached.

§ 101. The above considerations, of course, only apply to the chemically pure substances alcohol and water; how far the sugar, caramel, fusel, essences &c. of commercial spirits, and the innumerable substances in wines and beers may affect the solidification is a matter for future research. It is quite possible, for instance, that in some rums the 10 per cent. alcohol above that required for the cryohydrate might find sufficient foreign matter present to form therewith a solid, and so allow the whole to solidify.

§ 102. I believe that the detection of this 4-molecule hydrate of alcohol reconciles the apparently contradictory results of former experimenters. Thus, looking on wine as a 10-per-cent. spirit of wine, M. Melsens obtained by a freezing-mixture 40 per cent. of ice. I judge from Table XI. that the temperature reached was  $-8^{\circ}$ , if we make no allowance for loss of ice during manipulation.

§ 103. The evidence adduced by Messrs. Dupré, Page, and others points to the existence of at least one hydrate of alcohol; but I am not prepared to say that such hydrate is necessarily identical with the 4-molecule cryohydrate which we have been considering. It must be remembered in this connexion that the cryohydrates of solid salts contain more water than any other known hydrate; and the existence of the 4-molecule cryohydrate rather, I conceive, tends to show that the ordinary hydrate of alcohol contains less water, and is, as some of Dupré and others' experiments may be interpreted as showing, the 3-hydrate



*Cryohydrate of Ether.*

§ 104. *Cryohydrate of Ether* (?).—It is well known that when water and ethylic ether are shaken together mutual but only partial mixture ensues, the water taking up about one ninth of its volume of ether, and the ether about one thirty-sixth of its volume of water. Such an aqueous solution of ether when subjected to cold, solidifies at  $-2^{\circ}$  C., without any separation of ether, into a dry solid consisting of ether and water. The compound exhibits an interesting feature, inasmuch as it exemplifies the effect of cooling on the luminosity of flame. The cryohydrate of ether may be solidified in a long test-tube, and thence removed, presenting the appearance of a candle. One end of this is cut off flat, and the whole placed upright on a plate. A light being applied at the top, the whole melts away as the ether burns. The flame is quite non-luminous. The ether is only free to burn as it is in the act of melting ice, and is so cooled. So it is well known that marsh-gas becomes luminous if heated before combustion. Thus ether (which is empirically olefiant gas plus water) and alcohol (which is empirically ether plus water) have flames of luminosity the less according as their ratio of potential water is greater. The cryohydrate of ether is in fact physically, as far as its luminosity is concerned, an alcohol.

Throughout this second part of this research I have been much indebted to my friend Mr. R. Cowper for his very zealous and skilful assistance.

XXXI. *The Specific Heat of the Elements Carbon, Boron, and Silicon.*—Part I. *The Relation between the Specific Heat of these Elements in the free state and the Temperature.* By Dr. H. FRIEDRICH WEBER, *Professor of Physics and Mathematics.*

[Concluded from p. 183.]

B. *Specific Heat of Graphite.*

KOPP has put forward the theory that all modifications of carbon possess the same specific heat\*; but he has not tested this theory by experiment. All the forms of carbon except diamond are more or less porous, and therefore absorb varying quantities of gas; hence an error is introduced in determining their specific heats. In order to test Kopp's hypothesis I carried out the following experiments. I first of all sought to determine whether any thermal change occurs when graphite and water are brought into contact, the initial temperature of each being the same. A piece of pure graphite weighing 3.51

\* *Ann. der Chem. und Pharm.* Ser. 3, vol. cxli. p. 121.



grms. was placed in the inner of two long test-tubes, which were then sunk to the neck in the ice of an ice-calorimeter: a stopper of cotton-wool prevented the outer air from coming into contact with the graphite. As the graphite was gradually cooled down the motion of the mercury thread was carefully noted, with the result that the forward movement was equal to 0.11 division per minute. When the temperature of the graphite was 0° it was quickly removed and placed in the receiving-vessel of the calorimeter, and the movement of the mercury thread again carefully noted. The forward movement was exactly the same as that noticed before the introduction of the graphite; hence it follows that there is not the smallest evolution of heat from the contact of graphite with water. Another experiment proved that the amount of gas absorbed by 3 grms. of lamellar graphite did not alter the weight of the mass so much as one milligramme.

The following experiments were carried out with a piece of very pure lamellar graphite from Ceylon. The percentage of ash in this sample of graphite was 0.38; the numbers deduced for the specific heat will therefore hold good for absolutely pure graphite within 1 or 2 units in the fourth decimal place. I did not determine the hydrogen which was possibly present, as Kopp has found that the amount of this element in Ceylon graphite is exceedingly small, varying from .06 to .17 per cent.

*a. Experiments carried on at ordinary Temperatures with the help of the Ice-calorimeter.*

First Series.

$$N_0 = 10.24.$$

G.	T.	N.	W.	C <sub>0</sub> -T.
3.718	-79.35	366.0	-35.74	0.1212
3.718	-79.20	367.2	-35.87	0.1218
3.718	-79.30	370.2	-35.17	0.1227
3.718	-79.28	367.8	-35.93	0.1219
$W_{-79.3}^{0.0} = 9.664.$				
Second Series.				
$N_0 = 10.24.$				
3.718	-21.52	117.0	-11.42	0.1428
3.718	-21.20	116.7	-11.40	0.1447
3.718	-21.35	118.0	-11.52	0.1451
3.718	-21.36	117.2	-11.44	0.1442
$W_{-21.4}^{0.0} = 3.076.$				

Table (continued).

Third Series.

$$N_0 = 9.80.$$

G.	T.	N.	W.	C <sub>0</sub> -T.
3.718	21.65	127.0	12.96	0.1610
3.718	21.55	125.9	12.84	0.1603
3.718	21.60	126.0	12.86	0.1601
3.718	21.60	126.3	12.89	0.1605
$W_0^{21.6} = 3.465.$				
Fourth Series.				
$N_0 = 9.80.$				
3.55	98.65	654.4	66.77	0.1907
3.55	99.10	656.8	67.02	0.1905
3.55	99.25	655.9	66.93	0.1900
3.55	99.0	655.7	66.91	0.1904
$W_0^{99.0} = 18.85.$				
Fifth Series.				
$N_0 = 9.80.$				
1.625	177.2	616.3	62.89	0.2184
1.625	177.8	620.2	63.29	0.2191
1.623	179.0	622.5	63.52	0.2187
1.624	178.0	619.7	63.23	0.2187
$W_0^{178.0} = 38.93.$				
Sixth Series.				
$N_0 = 9.80.$				
1.258	226.5	657.2	67.06	0.2354
1.257	225.4	652.4	66.57	0.2348
1.250	224.1	644.5	65.57	0.2348
1.255	225.3	651.7	66.47	0.2350
$W_0^{225.3} = 52.96.$				

Table (continued).

Seventh Series.

$N_0 = 9.80$ .

G.	T.	N.	W.	C <sub>0-T</sub> .
1.250	274.1	843.2	86.04	0.2511
1.242	273.6	834.2	85.12	0.2505
1.240	271.9	829.0	84.59	0.2509
1.244	273.2	835.5	85.25	0.2508
$W_0^{273.2} = 68.53$				

From the average results of these seven series of experiments the following values for the specific heat of graphite are deduced :—

		Values of $\frac{\Delta y}{\Delta T}$
$y_{-50.3} = \frac{W_{-79.3}^{0.0} - W_{-21.4}^{0.0}}{57.9} = 0.1138$	}	..... 0.000749.
$y_{-10.7} = \frac{W_{-21.4}^{0.0}}{21.4} = 0.1437$		..... 0.000777.
$y_{10.8} = \frac{W_{0.0}^{21.6}}{21.6} = 0.1604$	}	..... 0.000764.
$y_{61.3} = \frac{W_{0.0}^{99.0} - W_{0.0}^{21.6}}{77.4} = 0.1990$		..... 0.000715.
$y_{138.5} = \frac{W_{0.0}^{178.0} - W_{0.0}^{99.0}}{79.0} = 0.2542$	}	..... 0.000672.
$y_{201.6} = \frac{W_{0.0}^{225.3} - W_{0.0}^{178.0}}{47.3} = 0.2966$		..... 0.000596.
$y_{249.3} = \frac{W_{0.0}^{273.2} - W_{0.0}^{225.3}}{47.9} = 0.3250$		

Graphite, therefore behaves in a manner exactly analogous with diamond; its specific heat notably increases with increasing temperature. This increase shows an acceleration from  $-50^\circ$  to  $0^\circ$ ; from  $0^\circ$  to  $250^\circ$  it diminishes. The curve of the specific heat of graphite shows, therefore, a turning-point in the neighbourhood of  $0^\circ$ . The small change in the value of  $\frac{\Delta y}{\Delta T}$  when T is about  $= 0^\circ$ , makes it evident that great care must be exercised

in experiments performed with the object of determining the exact temperature at which this point occurs. The steady decrease from 0° to 250° in the value of  $\frac{\Delta y}{\Delta T}$  makes it almost certain

that the specific heat of graphite, as that of diamond, is expressed by a constant number at higher temperatures. Inasmuch as it appears that, in the curves expressing the specific heats of diamond and of graphite, the value of the difference  $y_T$  (graphite)  $-y_T$  (diamond) becomes smaller and smaller as  $T$  increases (within the interval  $T = +50^\circ$  to  $T = 250^\circ$ ); and as a series of other elements exhibits the same specific heats in all their modifications, it is probable that the constant values which express the specific heats of diamond and graphite at high temperatures are identical.

A determination of the specific heat of graphite for the temperatures 500° to 1000° has completely fulfilled both of these expectations: the following Tables give the results of this determination.

### b. *Experiments at High Temperatures with the double Calorimeter.*

### Eighth Series.

	G.	Q.	$\Delta t$ .	W.	$\Delta T$ .	$CT_0 - T$ .	$T_0$ .
Platinum...	32.390	153.21	3.920	600.5	535.2	0.03465	22.10
Graphite ...	3.370	153.50	3.820	586.3		0.3251	22.00
Platinum...	32.390	151.22	3.845	581.4	519.2	0.03459	21.74
Graphite ...	3.368	152.41	3.715	566.1		0.3237	21.60

From the first experiments ...  $W_{22.0}^{557.2} = 174.0$ .

From the second experiments  $W_{21.6}^{540.8} = 168.1$ .

### Ninth Series.

Platinum...	32.390	153.44	5.385	826.3	720.2	0.03541	22.38
Graphite ...	3.260	154.03	5.450	839.4		0.3574	22.45
Platinum...	32.390	150.32	5.367	806.7	705.0	0.03535	22.12
Graphite...	3.211	151.04	5.315	802.7		0.3549	22.06

From the first experiments ...  $W_{22.4}^{742.6} = 257.5$ .

From the second experiments  $W_{22.1}^{727.0} = 250.0$ .

Table (continued).

Tenth Series.

	G.	Q.	$\Delta t$ .	W.	$\Delta T$ .	$CT_0-T$ .	$T_0$ .
Platinum...	32.390	204.20	5.156	1053.0	899.3	0.03615	22.74
Graphite...	3.186	204.92	5.266	1079.0		0.3769	22.81
Platinum...	32.390	201.42	5.069	1020.9	874.8	0.03604	21.62
Graphite...	3.120	200.10	5.105	1021.5		0.3742	21.67

From the first experiments ...  $W_{22.8}^{922.1} = 338.7$ .

From the second experiments  $W_{21.7}^{896.5} = 327.4$ .

Eleventh Series.

Platinum...	32.390	250.30	4.830	1209.0	1018.7	0.03664	22.41
Graphite...	3.102	252.10	4.853	1223.5		0.3872	22.38
Platinum...	32.390	251.51	4.860	1222.4	1028.9	0.03668	22.83
Graphite...	3.063	249.40	4.906	1223.7		0.3886	22.96

From the first experiments ...  $W_{22.4}^{1041.1} = 394.4$ .

From the second experiments  $W_{23.0}^{1051.9} = 399.5$ .

These results may be reduced for an equal temperature-interval: we adopt the mean of all the lower values, namely  $22^{\circ}.2$ . As the specific heat of graphite at  $22^{\circ}.2 = 0.169$ , the following results are obtained:—

$$W_{22.2}^{557.2} = 174.0,$$

$$W_{22.2}^{742.6} = 257.5,$$

$$W_{22.2}^{922.1} = 338.6,$$

$$W_{22.2}^{1041.1} = 394.4,$$

$$W_{22.2}^{540.8} = 168.0,$$

$$W_{22.2}^{727.0} = 250.0,$$

$$W_{22.2}^{896.5} = 327.3,$$

$$W_{22.2}^{1051.9} = 399.6.$$

From these numbers we deduce:—

$$y_{649.0} = \frac{W_{22.2}^{742.6} - W_{22.2}^{557.2}}{185.4} = 0.4504,$$

$$y_{632.3} = \frac{W_{22.2}^{922.1} - W_{22.2}^{742.6}}{179.5} = 0.4518,$$

$$y_{981.6} = \frac{W_{22.2}^{1041.1} - W_{22.2}^{922.1}}{119.0} = 0.4688,$$

$$y_{633.9} = \frac{W_{22.2}^{727.0} - W_{22.2}^{540.8}}{186.2} = 0.4404,$$

$$y_{811.7} = \frac{W_{22.2}^{896.5} - W_{22.2}^{727.0}}{169.5} = 0.4560,$$

$$y_{974.2} = \frac{W_{22.2}^{1051.9} - W_{22.2}^{896.5}}{155.4} = 0.4652.$$

For the calculation of this  $y$ -value it is assumed that the specific heat of graphite, within the temperature-intervals  $550^{\circ}$  to  $750^{\circ}$ ,  $750^{\circ}$  to  $900^{\circ}$ , and  $900^{\circ}$  to  $1050^{\circ}$ , changes linearly with the temperature; it is therefore allowable to write

$$y_{649.9} + y_{633.9} = 2y_{641.9},$$

$$\&c, \qquad \&c,$$

and to deduce the following mean values:—

$$y_{641.9} = 0.4454,$$

$$y_{822.0} = 0.4539,$$

$$y_{977.9} = 0.4670.$$

A comparison of these numbers with those deduced for diamond, viz.

$$y_{606.7} = 0.4408,$$

$$y_{806.5} = 0.4489,$$

$$y_{985.0} = 0.4589,$$

leads to the following conclusions:—

(1) The increase of the specific heat with the temperature,

$\frac{\Delta y}{\Delta T}$ , is

	For graphite.	For diamond.
	0.0000472	0.0000405 between $600^{\circ}$ and $800^{\circ}$
	0.0000840	0.0000561 „ 800 „ 1000
Mean .	0.0000656	0.0000483

whether the values of  $\frac{\Delta y}{\Delta T}$ , for graphite and diamond, really increase within the temperature-interval  $600^{\circ}$  to  $1000^{\circ}$ , and whether the values are different for graphite and diamond, I cannot with certainty decide. An experimental error in the direct determination of  $W_{T_0}^T$ , amounting to 1 per cent. too much or too little, would influence the value assigned to  $y_T$  so as to falsify the true value of the quotient  $\frac{\Delta y}{\Delta T}$  as much as 100 per

cent. As the differences between the above four values of  $\frac{\Delta y}{\Delta T}$  amount at the most to 50 per cent. of the value of this expression, and as the magnitude of  $W_{T_0}^T$  is not determined to within less than  $\frac{1}{2}$  per cent. of its value, the magnitude of  $\frac{\Delta y}{\Delta T}$  may very well be independent of the temperature from  $600^{\circ}$  and upwards; and the value of this expression may be exactly the same for both modifications of carbon. Inasmuch, however, as the experi-

mental methods were not delicate enough to determine this question with precision, it is safer to deduce from the foregoing results the following generalization only—that, from a red heat upwards, the specific heat of carbon does not vary more than the specific heats of those elements which fulfil the law of Dulong and Petit. Thus Bedé\* shows that the specific heats of the following elements for the temperatures T are

$$\begin{aligned}\text{Copper} &= 0.0910 + 0.000046T, \\ \text{Zinc} &= 0.0865 + 0.000088T, \\ \text{Lead} &= 0.0286 + 0.000038T.\end{aligned}$$

(2) The specific heats of graphite and diamond are identical from the temperature 600° and upwards (there are slight divergencies, but they do not exceed  $\frac{1}{2}$  to 2 per cent. of the value of  $y$ ). By reducing, by the help of the mean differential quotient  $\frac{\Delta y}{\Delta T} = 0.000656$ , the above values for the specific heat of graphite to the temperatures 606°·7, 806°·5, and 985°·0, and comparing these with the specific heat of diamond at the same temperatures, we obtain the numbers

	Graphite.	Diamond.	Difference.
$y_{606.7}$	$= 0.4431$	$0.4408$	$0.0023,$
$y_{806.5}$	$= 0.4529$	$0.4489$	$0.0040,$
$y_{985.0}$	$= 0.4674$	$0.4589$	$0.0085.$

Although the small difference increases with an increasing temperature, nevertheless it is not greater than the difference between the specific heats of different modifications of other elements. Thus, according to Regnault, the mean specific heats between 10° and 100° for steel and copper are

Soft steel $= 0.1165$		Soft copper $= 0.0948$
Hard steel $= 0.1175$		Hard copper $= 0.0934$

These differences may be accounted for by the varying molecular aggregation of the substances; and it may be accepted as true that from a red heat and upwards there is no real difference between the specific heat of the graphitic and that of the diamond modification of carbon. Inasmuch as this result appears to me one of great importance, both as regards the specific heat of the elements in general and that of the modifications of carbon in particular, I have sought to answer the question as to the difference or identity of the specific heats of graphite and diamond in another and somewhat simpler manner.

On the supposition that the specific heats of graphite and dia-

\* *Mém. Cour. de l'Acad. de Brux.* vol. xxvii.

mond are identical for every value of the temperature  $T$ , and representing the amounts of heat given up by 1 grm. of graphite and 1 grm. of diamond when cooled from  $T_1, T_2$ , &c. to  $T_0$  (where  $T_1, T_2$ , &c.  $> T_0$ ) by the series

$$W_g^{T_1-T_0}, W_g^{T_2-T_0}, W_g^{T_3-T_0}, \dots$$

and

$$W_d^{T_1-T_0}, W_d^{T_2-T_0}, W_d^{T_3-T_0}, \dots$$

the following equations hold good:—

$$W_g^{T_2-T_0} - W_g^{T_1-T_0} = W_d^{T_2-T_0} - W_d^{T_1-T_0},$$

$$W_g^{T_3-T_0} - W_g^{T_2-T_0} = W_d^{T_3-T_0} - W_d^{T_2-T_0}.$$

The following experiments prove that these equations may be accepted as expressing actual facts.

3·3 grms. of graphite were placed in one of the platinum vessels already described, and 3·5 grms. of diamond in the other. When these were heated to the same temperature they were brought into the double calorimeter and allowed there to cool.

#### First Experiment.

Heated to about 550°.

	G.	Q.	$\Delta t$ .	W.	$T_0$ .
Graphite.....	3·330	123·10	4·278	526·6	21·42
Diamond ...	3·512	125·81	4·150	522·2	21·33

#### Second Experiment.

Heated to about 750°.

Graphite.....	3·362	151·11	5·224	789·4	21·63
Diamond ...	3·525	153·40	5·172	793·5	21·58

#### Third Experiment.

Heated to about 1000°.

Graphite.....	3·401	203·22	5·607	1139·5	21·30
Diamond ...	3·541	203·13	5·658	1149·3	24·41

The amounts of heat given up by 1 grm. of graphite and 1 grm. of diamond respectively in cooling from about 550°, 750°, and 1000° to about 21°·5 were therefore

Graphite.	Diamond.
158·14 . . . .	148·72
234·82 . . . .	225·11
335·05 . . . .	324·56



The differences of the two consecutive numbers in these series are

For graphite.	For diamond.
76·68 . . . .	76·39
100·23 . . . .	99·45

As the differences for graphite are  $\left. \begin{array}{l} 0\cdot29 \\ 0\cdot78 \end{array} \right\}$  greater than those for diamond, these new experiments show that the specific heat of graphite is a very little greater than that of diamond, viz.

0·0020 between 550 and 750,  
0·0031 „ 750 „ 1000.

This agrees with the previously obtained results.

(3) The results

Graphite.	Diamond.
$\gamma_{606\cdot7} = 0\cdot4431,$	0·4408,
$\gamma_{806\cdot5} = 0\cdot4529,$	0·4489,
$\gamma_{985\cdot0} = 0\cdot4674,$	0·4589,

show that, from the point (about 600°) at which the specific heat of carbon ceases to vary with increase of temperature and becomes comparable with that of other elements, any real difference in the specific heats of the two modifications disappears, and carbon obeys the law of Dulong and Petit.

By multiplying the values obtained for the specific heat of carbon between 600° and 1000° by the generally received atomic weight 12 (deduced from the vapour-density of carbon compounds), we obtain a product varying from 5·4 to 5·6, which agrees with the atomic heat of those other elements which have small atomic weights (aluminium 5·7, phosphorus 5·5, sulphur 5·5, &c.).

*All the anomalies in the specific heat of carbon disappear when the temperature reaches a red heat.*

The results which I have obtained are not in keeping with those of Dewar\*, who obtained for gas-carbon the number 0·314 as representing the mean specific heat from 20° to 1040°, for graphite 0·310, and for diamond 0·366. For the mean specific heat of "carbon" between 20° and the temperature of the oxygen-hydrogen blowpipe (estimated at 2100°) Dewar obtained the number 0·374.

From these numbers Dewar concludes that "the true specific

\* British Association Reports, 1872, and Phil. Mag. December 1872.

heat of carbon at  $2000^{\circ}$  must be at least  $0.5$ ; so that at this temperature carbon would agree with the law of Dulong and Petit."

By comparing the mean values  $\int_{22.6}^{1046.4} ydT = 0.3879$  for graphite,

and  $\int_{22.4}^{1051.2} ydT = 0.3776$  for diamond, obtained by me with

Dewar's numbers; considerable differences are disclosed. All my experiments show that the mean value of the specific heat of graphite is somewhat *greater* than that of diamond: the direct results detailed on p. 284 establish the truth of this statement. Some cause of error has probably crept into Dewar's experiments; one of these causes may be the omitting to measure the exact temperature of the carbon when it was thrown into the calorimeter, this temperature being taken as equal to that of molten zinc. The temperature of the carbon must, however, have been rather less than  $1040^{\circ}$ , inasmuch as the heating-vessel was furnished on its outer rim with an iron disk (to shield it from zinc oxide); and as this disk was much cooler than the vessel itself, heat must have been lost in carrying the apparatus to the calorimeter. Whether this error was large enough to lower the specific heat of carbon between  $20^{\circ}$  and  $1000^{\circ}$  from  $0.388$  to  $0.310$ , or whether there were other errors also present, I cannot undertake to say. I am inclined to place a greater degree of confidence in my own experiments, inasmuch as the temperature of the substance at the moment when it fell into the calorimeter was determined with the greatest accuracy. The expectation that, "starting from absolute zero, carbon or graphite most probably increases regularly in specific heat, whereas diamond probably diminishes until we reach  $-42^{\circ}3$  C., and then increases regularly until it exceeds that of graphite, which it continues to do until they agree at very high temperatures," has been fully realized in the case of graphite only: the variations in the specific heat of diamond are much simpler than Dewar supposed.

### C. The Specific Heat of dense amorphous Carbon.

The following Tables show the results of experiments upon a sample of dense carbon contained in the limestone of Wundsiedel in the Fichtelgebirge: this carbon was but little less dense than lamellar graphite; it left but  $0.33$  per cent, of ash.

First Series.

$$N_0 = 9.881.$$

G.	T.	N.	W.	$C_{0-T}$ .
0.677	98.9	123.9	12.54	0.1903
0.677	99.0	126.4	12.79	0.1909
Mean specific heat between 0° and 99° = 0.1906.				
Second Series.				
$N_0 = 9.881.$				
0.677	227.1	356.2	36.05	0.2345
0.671	224.0	347.7	35.19	0.2341
Mean specific heat between 0° and 225° = 0.2348.				

For graphite the numbers were

$$\left. \begin{aligned} C_{0-99.0} &= 0.1904, \\ C_{0-225.3} &= 0.2350. \end{aligned} \right\}$$

This specimen of amorphous carbon has therefore the same specific heat as graphite for the temperature-interval 0° to 225°.

*D. The Specific Heat of porous Wood Charcoal.*

The numbers hitherto obtained for the specific heat of porous carbon, viz.

$$C_{0-15^\circ} = 0.165 \text{ (De la Rive and Marcet—method of cooling),}$$

$$C_{18^\circ-98^\circ} = 0.241 \text{ (Regnault—method of mixtures),}$$

lead to the probable conclusion that the specific heat of this variety of carbon is identical with that of graphite, and that the contradictory result of Regnault was due to the evolution of heat by the contact of the porous substance with water. In order to determine the specific heat of porous carbon with the greatest possible accuracy the following experiments were carried out. The middle part (about 2 centims. long) of a thin glass tube of known weight was filled with porous carbon which had been washed in acid, and at the ends of the carbon cylinder the tube was narrowed so as to be only about 2 millims. in diameter. The tube was now heated to slight redness for fifteen minutes, a stream of chlorine being passed through it to remove the hydrogen contained in the carbon. Both ends of the tube were

now quickly sealed and the weight determined. The weight of the glass tube was 1.105 grm., and that of the enclosed porous carbon 1.410 grm. A platinum spiral weighing 0.655 grm. served as a weight to sink the tube under the water in an ice-calorimeter. The specific heat of the platinum spiral between  $0^\circ$  and  $T$  was  $C_{0-T} = 0.0319 + 0.000004T$ . The mean specific heat of the glass employed was from  $0^\circ$  to  $24^\circ = 0.1880$ ,  $0^\circ$  to  $99^\circ = 0.2017$ ,  $0^\circ$  to  $203^\circ = 0.2103$ ,  $0^\circ$  to  $256^\circ = 0.2136$ . From the following tabulated results the amounts of heat given up by the porous carbon, the glass, and the platinum spiral, in cooling from  $23^\circ$ ,  $99^\circ$ , and  $224^\circ$  to  $0^\circ$ , are obtained; and from these and the data already given the specific heat of porous carbon for the above-mentioned temperature-intervals are deduced.

## First Series.

$$N_0 = 9.881.$$

	G.	T.	N.	W.	$C_{0-123}$
Carbon .....	1.410	} 23.1	105.7	10.698	0.1663
Glass .....	1.105				0.1880
Platinum .....	0.655				0.0320
Carbon .....	1.410	} 23.9	108.9	11.020	0.1647
Glass .....	1.105				0.1880
Platinum .....	0.655				0.0320
Carbon .....	1.410	} 23.4	106.6	10.792	0.1650
Glass .....	1.105				0.1880
Platinum .....	0.655				0.0320

Mean specific heat of porous carbon between  $0^\circ$  and  $23.5^\circ = 0.1653$ .

## Second Series.

$$N_0 = 9.981.$$

$$C_{0-100}$$

Carbon .....	1.410	} 99.10	506.1	51.22	0.1935
Glass .....	1.105				0.2017
Platinum .....	0.655				0.0323
Carbon .....	1.410	} 99.25	505.8	51.19	0.1928
Glass .....	1.105				0.2017
Platinum .....	0.655				0.0323
Carbon .....	1.410	} 99.30	508.2	51.44	0.1943
Glass .....	1.105				0.2017
Platinum .....	0.655				0.0323

Mean specific heat of porous carbon between  $0^\circ$  and  $99.22^\circ = 0.1935$ .

Table (*continued*).

Third Series.

$$N_0 = 6.030.$$

	G.	T.	N.	W.	Co <sub>-223°</sub>
Carbon .....	1.410	} 224.0	800.2	132.7 {	0.2391
Glass .....	1.105				0.2116
Platinum .....	0.655				0.0328
Carbon' .....	1.410	} 221.6	790.4	131.1 {	0.2386
Glass .....	1.105				0.2114
Platinum .....	0.655				0.0328
Carbon .....	1.410	} 225.3	802.3	133.1 {	0.2377
Glass .....	1.105				0.2117
Platinum .....	0.655				0.0328
Mean specific heat of porous carbon between 0° and 223°·6 = 0.2385.					

By comparing these numbers with those expressing the specific heats of lamellar graphite and of dense carbon we have:—

Lamellar graphite.	Dense amorphous carbon.	Porous carbon.
C <sub>0-21.6</sub> = 0.1605	—	C <sub>0-23.5</sub> = 0.1653
C <sub>0-99.0</sub> = 0.1904	C <sub>0-99.0</sub> = 0.1906	C <sub>0-99.2</sub> = 0.1935
C <sub>0-225.3</sub> = 0.2350	C <sub>0-225.8</sub> = 0.2340	C <sub>0-233.6</sub> = 0.2385

From these it may be concluded that *the specific heats of graphite, of dense amorphous carbon, and of porous carbon are identical within the temperature-interval 0° to 225°*. Although the numbers obtained for graphite and for porous carbon differ so much as 2 to 3 per cent. of their value, yet these discrepancies may be accounted for by the difference in the conditions of the two substances. To determine, however, to what cause these differences are really due requires more delicate experiments with absolutely pure substance.

From Regnault's experiments it appeared that as many thermally different modifications of carbon exist as there are physically different modifications. The above results, however, show that this is not the case, and that, from a thermal point of view, there are but two really different modifications of carbon, the transparent (diamond) and the opaque (graphite, dense and porous carbon). The high numbers obtained by Regnault,

$$C_{18^{\circ}-98^{\circ}} = 0.2415 \text{ for wood carbon,}$$

$$C_{19^{\circ}-90^{\circ}} = 0.2608 \text{ for animal carbon,}$$

are only to be accounted for (as Regnault himself suggests) by the supposition that heat is evolved when the porous carbon comes into contact with the water of the calorimeter. That a considerable amount of heat is thus really evolved (an amount sufficient, if taken into account, to reduce Regnault's number to the real number, viz. 0.1935 for porous carbon,  $C_{0^{\circ}-99^{\circ}}$ ) appears from the following experiment.

The glass tube containing the porous carbon used in the fore-mentioned experiments was drawn out at one end and then broken so as to have an orifice about 1 millim. wide. The tube was heated to  $99^{\circ}.1$  for forty-five minutes, and then quickly plunged into the ice-calorimeter; the water in the calorimeter rose in the tube so as to wet the carbon. The circumstance that in this experiment the mercury thread did not come to rest for thirty-two minutes, while at other times after twelve to fifteen minutes no further movement was observable, showed that an evolution of heat followed upon the wetting of the porous carbon by the water. This becomes more evident from the following data:—

1.410 grm. carbon	} cooled from $99^{\circ}.1$ to $0^{\circ}$ , during which time the car- bon was wetted with water,	} gave up 57.06 heat- units in the calori- meter.
1.104 grm. glass		
0.655 grm. platinum		

From these numbers, and from the known mean specific heats of the glass and platinum employed ( $C_{0^{\circ}-99^{\circ}.1} = 0.2017$  and  $0.02323$  respectively), the number  $C_{0^{\circ}-99^{\circ}.1} = 0.2355$  is deduced as the mean specific heat of the porous carbon wetted in the calorimeter, a number which agrees very well with Regnault's  $C_{18^{\circ}-98^{\circ}} = 0.2415$ . The above experiment gives for porous unwetted carbon the number  $C_{0^{\circ}-99^{\circ}.2} = 0.1935$ . *A unit weight of porous carbon, as far as possible free from water, evolves 4.16 heat-units when wetted with water.*

### III. THE SPECIFIC HEAT OF CRYSTALLIZED BORON.

Two hundred small octahedral crystals of boron, kindly given by Professor Rammelsberg, were used. These crystals, having been prepared by heating boric acid with aluminium, could not be considered perfectly pure. The total weight of boron was 671 milligrams. The substance was placed on a small vessel of tinfoil weighing not more than 0.1 grm. On account of the small weight of this tinfoil and its relatively low specific heat, it was possible to determine the specific heat of the boron with

great accuracy. The mean specific heat of the tin-foil used between  $0^{\circ}$  and  $T$ ,  $C_{0-T}$ , was determined from a number of experiments in which  $T$  varied from  $-21^{\circ}$  to  $+200^{\circ}$ , and was represented by the expression

$$C_{0-T} = 0.0533 + 0.00002346 T.$$

After each experiment the crystals were removed from the tin-foil vessel, dried, and placed in a new vessel. In the last experiment, where the boron was heated to a temperature above the melting-point of the tin-foil, a vessel of glass, the mean specific heat of which from  $0^{\circ}$  to  $263^{\circ}$  was 0.2141, was employed.

First Series.

$$N_0 = 10.202.$$

	G.	T.	N.	W.	$C_{-79-0}$
Boron .....	0.667	-79.0	107.0	-10.49	0.1910
Tin-foil .....	0.103				0.0528
Boron .....	0.667	-79.4	108.5	-10.58	0.1918
Tin-foil .....	0.101				0.0528
Boron .....	0.662	-79.3	107.1	-10.50	0.1917
Tin-foil .....	0.104				0.0528
Mean .....	.....	-79.2	.....	.....	0.1915
$W_{-79.2}^0 = 15.166.$					
Second Series.					
$N_0 = 10.202.$					
					$C_{0-53}$
Boron .....	0.671	53.25	89.5	8.794	0.2379
Tin-foil .....	0.102				0.0549
Boron .....	0.668	53.95	91.1	8.931	0.2396
Tin-foil .....	0.100				0.0549
Boron .....	0.667	52.75	88.0	8.628	0.2371
Tin-foil .....	0.098				0.0549
Mean .....	.....	53.32	.....	.....	0.2382
$W_0^{53.32} = 12.701.$					

Table (continued).

Third Series.

 $N_0 = 10.202.$ 

	G.	T.	N.	W.	$C_{0-100}$
Boron.....	0.665	100.30	178.6	17.510	0.2542
Tinfoil.....	0.100				0.0556
Boron.....	0.664	100.05	178.3	17.480	0.2549
Tinfoil.....	0.102				0.0556
Boron.....	0.664	99.85	178.6	17.511	0.2553
Tinfoil.....	0.105				0.0556
Mean .....	.....	100.06	.....	.....	0.2548
$W_0^{100.06} = 25.495.$					
Fourth Series.					
$N_0 = 10.202.$					$C_{0-152}$
Boron.....	0.664	150.6	287.2	28.162	0.2730
Tinfoil.....	0.101				0.0568
Boron.....	0.664	151.2	288.1	28.244	0.2726
Tinfoil.....	0.102				0.0568
Boron.....	0.662	153.0	290.0	28.428	0.2720
Tinfoil.....	0.100				0.0568
Mean .....	.....	151.6	.....	.....	0.2725
$W_0^{151.6} = 41.311.$					
Fifth Series.					
$N_0 = 10.202.$					$C_{0-203}$
Boron.....	0.660	201.2	403.7	39.580	0.2891
Tinfoil.....	0.103				0.0580
Boron.....	0.660	203.0	408.0	39.997	0.2894
Tinfoil.....	0.104				0.0580
Boron.....	0.657	204.5	407.6	39.959	0.2885
Tinfoil.....	0.101				0.0580
Mean .....	.....	202.9	.....	.....	0.2890
$W_0^{202.9} = 58.638.$					



Table (continued).

Sixth Series

 $N_0 = 6.030$ .

	G.	T.	N.	W.	C <sub>0-264</sub> .
Boron.....	0.651	265.6	449.2	74.50	0.3075
Glass .....	0.375				0.2142
Boron.....	0.651	263.4	443.8	73.59	0.3058
Glass .....	0.375				0.2141
Boron.....	0.642	261.8	437.9	72.62	0.3071
Glass .....	0.384				0.2141
Mean .....	.....	263.6	.....	.....	0.3068
$W_0^{263.6} = 80.872$ .					

From these values of  $W$  the following values for the specific heat of boron are deduced:—

$y_{-39.6} = \frac{W_{-79.2}^{0.0}}{79.2} = 0.1915$	} Values of $\frac{\Delta y}{\Delta T}$	0.000706 from $-40^\circ$ to $+25^\circ$ .
$y_{26.6} = \frac{W_{53.32}^{53.32}}{53.32} = 0.2382$		
$y_{76.7} = \frac{W_{0.0}^{100.06} - W_{0.0}^{53.32}}{46.74} = 0.2737$	} 0.000708 from $25^\circ$ to $75^\circ$ .	
$y_{125.8} = \frac{W_{0.0}^{151.6} - W_{0.0}^{100.06}}{51.54} = 0.3069$		
$y_{177.2} = \frac{W_{0.0}^{202.9} - W_{0.0}^{151.6}}{51.3} = 0.3378$	} 0.000601 from $125^\circ$ to $175^\circ$ .	
$y_{233.2} = \frac{W_{0.0}^{263.6} - W_{0.0}^{202.9}}{60.7} = 0.3663$		
		0.000508 from $175^\circ$ to $230^\circ$ .

These results show that the specific heat of crystalline boron varies, within the temperature-interval  $-80^\circ$  to  $+260^\circ$ , in a manner exactly analogous with that of the variation of the specific heats of both modifications of carbon. As with these, so in the case of boron there appears to be an inflection-point in the neighbourhood of  $0^\circ$ . The wonderful agreement between the variation in the specific heats of boron and carbon from  $-80^\circ$  to  $+260^\circ$  makes it almost certain that at higher temperatures

the value of the specific heat of the former, as we have shown to be the case with the latter, is a constant number.

The results of the determination detailed above may be very exactly represented by the following expression, in their relation to the temperature  $T$  measured from absolute zero:—

$$y_T = A - \frac{B(1 + aT)}{qT^e}.$$

( $A, B, a, q = \text{constants}$ ;  $A > B$ ;  $q > a$ .) On the supposition that this expression represents the relation of the specific heat to the temperature for temperatures  $< -80^\circ$  and  $> 260^\circ$  (measured from the ordinary zero),  $A - B$  will represent the limit of value attained by the specific heat of boron at low temperatures, and  $A$  will represent the final constant value attained at high temperatures. The value of  $A$  calculated from the above equation is about 0.49; this may be attained at a medium red heat. From an inspection of the curve (Pl. VII.) representing the specific heat of boron between  $-40^\circ$  and  $+230^\circ$ , it will be seen that in the dotted part a value of about 0.50 is attained.

As soon as I can obtain 2 or 3 grms. of pure boron I shall continue my experiments with the view of testing the accuracy of the above anticipation. Considering the rapid increase in the value of the specific heat of boron as the temperature increases until a certain point is reached, and the gradual diminution in the velocity of this increase after that point, I feel justified in concluding that it is very probable indeed that at higher temperatures the specific heat attains a constant value represented (in round numbers) by the fraction 0.50, and that therefore the number 11, which is generally accepted as the atomic weight of boron, is really the atomic weight; further, that the atomic heat of boron is about 5.5, and that therefore *at a red heat boron obeys the law of Dulong and Petit*.

#### IV. THE SPECIFIC HEAT OF CRYSTALLIZED SILICON.

1.123 grm. of material was used; it consisted of small brilliant steel-grey crystals, which were prepared in Professor Ram-melsberg's laboratory by reducing silicon-calcium fluoride with zinc and sodium. The results of a first series of experiments, in which the silicon was enclosed in a glass vessel, were rejected, and another series was undertaken in which a vessel of tinfoil weighing about 0.2 grm. was employed. After each experiment the crystals were removed, dried at  $150^\circ$ , and placed in a fresh vessel; the weight of the material gradually decreased from 1.123 to 1.045 grm. A platinum spiral which was used as a sinker weighed 0.501 grm., and had a mean specific heat between  $0^\circ$  and  $T$  equal to  $0.0319 + 0.000004T$ .

First Series.

$$N_0 = 14.42.$$

	G.	T.	N.	W.	C <sub>-80-0</sub>
Silicon .....	1.052	-79.9	200.6	-13.631	0.1371
Tinfoil .....	0.203				0.0528
Platinum ...	0.501				0.0317
Silicon .....	1.050	-79.6	194.5	-13.492	0.1359
Tinfoil .....	0.211				0.0529
Platinum.....	0.501				0.0317
Silicon .....	1.045	-79.6	192.6	-13.333	0.1351
Tinfoil .....	0.202				0.0528
Platinum ...	0.501				0.0317
Mean .....	.....	-79.7	.....	.....	0.0360

$$W_{-79.7}^{0.0} = 10.839.$$

Second Series.

$$N_0 = 14.42.$$

$$C_{0-43}$$

Silicon .....	1.123	42.9	134.9	9.361	0.1700
Tinfoil .....	0.205				0.0548
Platinum ...	0.501				0.0321
Silicon .....	1.120	43.5	136.8	9.491	0.1702
Tinfoil .....	0.210				0.0548
Platinum ...	0.501				0.0321
Silicon .....	1.113	43.0	133.3	9.247	0.1690
Tinfoil .....	0.198				0.0548
Platinum ...	0.501				0.0321
Mean .....	.....	43.13	.....	.....	0.1697

$$W_0^{43.13} = 7.319.$$

Third Series.

$$N_0 = 14.42.$$

$$C_{0-71}$$

Silicon .....	1.104	71.3	227.2	15.757	0.1755
Tinfoil .....	0.202				0.0552
Platinum.....	0.501				0.0322
Silicon .....	1.104	70.8	224.5	15.569	0.1741
Tinfoil .....	0.210				0.0552
Platinum.....	0.501				0.0322
Silicon .....	1.100	71.1	225.8	15.663	0.1753
Tinfoil .....	0.206				0.0552
Platinum.....	0.501				0.0322
Mean .....	.....	71.07	.....	.....	0.1750

$$W_0^{71.07} = 12.441.$$

Table (continued).

Fourth Series.

$$N_0 = 14.42.$$

	G.	T.	N.	W.	$C_{0-101}$
Silicon.....	1.096	101.2	327.6	22.719	0.1795
Tinfoil.....	0.210				0.0556
Platinum.....	0.501				0.0323
Silicon.....	1.094	100.7	326.5	22.637	0.1801
Tinfoil.....	0.205				0.0556
Platinum.....	0.501				0.0323
Silicon.....	1.091	100.8	324.1	22.478	0.1789
Tinfoil.....	0.202				0.0556
Platinum.....	0.501				0.0323
Mean .....	.....	100.9	.....	.....	0.1795

$$W_0^{100.9} = 18.111.$$

Fifth Series.

$$N_0 = 14.42.$$

 $C_{0-157}$ 

Silicon .....	1.088	156.6	518.7	35.971	0.1854
Tinfoil .....	0.206				0.0569
Platinum.....	0.501				0.0325
Silicon .....	1.084	156.2	517.4	35.879	0.1862
Tinfoil .....	0.204				0.0569
Platinum.....	0.501				0.0325
Silicon .....	1.081	157.0	515.5	35.749	0.1850
Tinfoil .....	0.200				0.0569
Platinum.....	0.501				0.0325
Mean .....	.....	156.6	.....	.....	0.1855

$$W_0^{156.6} = 29.051.$$

Sixth Series.

$$N_0 = 14.42.$$

 $C_{0-212}$ 

Silicon .....	1.075	211.5	607.6	49.068	0.1894
Tinfoil .....	0.206				0.0583
Platinum.....	0.501				0.0327
Silicon .....	1.070	212.0	604.6	48.866	0.1891
Tinfoil .....	0.203				0.0583
Platinum.....	0.501				0.0327
Silicon .....	1.062	212.4	606.3	48.979	0.1903
Tinfoil .....	0.208				0.0583
Platinum.....	0.501				0.0327
Mean .....	.....	212.0	.....	.....	0.1896

$$W_0^{212.0} = 40.190.$$

Table (continued).

Seventh Series.

 $N_0 = 6.030$ .

	G.	T.	N.	W.	$C_{0-252}$
Silicon .....	1.060	} 251.6	468.6	77.720	{ 0.1924 0.2134 0.0329
Tinfoil .....	0.321				
Platinum .....	0.501				
Silicon .....	1.060	} 254.8	474.0	78.606	{ 0.1920 0.2136 0.0329
Tinfoil .....	0.321				
Platinum .....	0.501				
Silicon .....	1.055	} 250.6	426.5	70.741	{ 0.1908 0.2153 0.0329
Tinfoil .....	0.304				
Platinum .....	0.501				
Mean .....	.....	252.3	.....	.....	0.1917
$W_0^{252.3} = 48.366$ .					

From the values of  $W_0^T$  the following specific heats of crystallized silicon are deduced:—

$y_{-39.8} = \frac{W_{-79.7}^{0.0}}{79.7} = 0.1360$	Values of $\frac{\Delta y}{\Delta T}$ . 0.000550 from $-40^\circ$ to $+20^\circ$ . 0.000382 from $20^\circ$ to $60^\circ$ . 0.000235 from $60^\circ$ to $90^\circ$ . 0.000148 from $90^\circ$ to $130^\circ$ . 0.000085 from $130^\circ$ to $185^\circ$ . 0.000038 from $185^\circ$ to $230^\circ$ .
$y_{21.6} = \frac{W_{0.0}^{42.13}}{42.13} = 0.1697$	
$y_{57.1} = \frac{W_{0.0}^{71.07} W_{0.0}^{42.13}}{28.94} = 0.1833$	
$y_{86.0} = \frac{W_{0.0}^{100.9} - W_{0.0}^{71.07}}{29.83} = 0.1901$	
$y_{128.7} = \frac{W_{0.0}^{156.6} - W_{0.0}^{100.9}}{55.7} = 0.1964$	
$y_{184.3} = \frac{W_{0.0}^{212.0} - W_{0.0}^{156.6}}{55.4} = 0.2011$	
$y_{232.4} = \frac{W_{0.0}^{252.3} - W_{0.0}^{212.0}}{40.3} = 0.2029$	

From these experiments it is evident that the specific heat of silicon is a function of the temperature, and that at about  $200^\circ$  it attains a constant value. The variation in the specific heat of silicon in the neighbourhood of  $200^\circ$  is not greater than the variation in the case of the metallic elements. If the specific heat

of silicon increases from 200° to 300° in the same proportion as it does from 184° to 232°, it will attain the value 0.2055 at 300°. Multiplying this number by 28 (the atomic weight of silicon deduced in accordance with Avogadro's law), we obtain the number 5.75. This number is in keeping with those expressing the atomic heats of the metals. Then, taking Regnault's determination, we have the following atomic heats:—

5.8.	6.0.	6.1 to 6.3.		6.4 to 6.6.	
For aluminium.	Magnesium. Copper. Silver. .....	Nickel. Cobalt. Ir on .....	Osmium. Ruthenium. Palladium. .....	Platinum. Gold. Iridium. .....	Indium. Tin. &c. .....

*Silicon does not form an extraordinary exception to the law of Dulong and Petit; so soon as the temperature passes 200° it comes within the sphere of this law. From these experiments it also follows, that the smallest relative weight of silicon (28) hitherto found in the molecule of any of the gaseous compounds of this element is in reality the atomic weight of silicon.*

#### V. GENERAL RESULTS.

(1) The values of the specific heats of the elements carbon, boron, and silicon change with the temperature; these values gradually increase with an increase of temperature until a point is reached at which they are constant. This point is situated at about 600° for carbon and boron, at about 200° for silicon. The specific heat of carbon at 600° is about seven times, that of boron about two and a half times as great as at -50°. The nature of the function expressing the relation between the specific heat  $y_T$  and the temperature appears to be the same for the three elements, and to have the form

$$y_T = A - B \frac{1 + hT}{qT} \left| \begin{array}{l} A > B \\ q > h, \end{array} \right.$$

where A, B, q, and h represent positive quantities, and T the temperature calculated for absolute zero.

The specific heats of the elements are not, generally speaking, expressed by constant numbers, the physical condition of the elements influencing their specific heats as much as their chemical nature. The idea that the temperature exercises but an insignificant influence upon the magnitude of the specific heats of the elements, and that this influence may be overlooked with-

out introducing any serious error into the determination of the specific heat, may now no longer be entertained.

(2) The constant final values for the specific heats of carbon, boron, and silicon are, in round numbers, 0.46, 0.50, and 0.205 respectively. The products of these numbers, multiplied into the atomic weights 12, 11, and 28, are

5.5, 5.5, and 5.8,

values which are in keeping with the atomic heats of the metals and of the other non-metals. Carbon, boron, and silicon, which hitherto formed the most marked exceptions to the law of Dulong and Petit, are now shown to obey this law when a certain temperature is reached. This law may therefore be accepted as binding in the case of all the elements; it must, however, be formulated in a manner slightly differing from that ordinarily laid down. Thus the specific heats of the solid elements vary with the temperature; for every element, however, there is a point ( $T_0$ ) from which the variation in the specific heat with increasing temperature is entirely insignificant. The product of the atomic weight into the value of the specific heat (estimated at temperatures so that  $T > T_0$ ) is, for all the elements, a nearly constant number varying from 5.5 to 6.5.

The smallest relative quantities of the elements carbon, boron, and silicon hitherto found in the molecules of their gaseous compounds, viz. 12, 11, and 28, really represent the atomic weights of these elements.

(3) All opaque modifications of carbon (graphitic, dense and porous) have the same specific heats. From a thermal point of view there are, below a red heat, but two allotropic modifications of carbon, the opaque and the transparent. The specific heats of these two modifications differ considerably at low temperatures; with increasing temperatures, however, their values are gradually equalized, until at about  $600^\circ$  they become the same. A consideration of the specific heat of carbon tends to show that from a red heat upwards there are no different allotropic modifications of this element; from the point at which the *optical* difference between the two modifications of carbon lessens, the *thermal* difference begins to disappear also.

In the year 1864 Kopp deduced the rule that the different allotropic modifications of a substance have the same specific heats. The allotropic forms of carbon have hitherto stood in direct opposition to this rule; now, however, it is proved that from a certain temperature those modifications obey Kopp's rule.

## VI. FURTHER PROBLEMS.

The foregoing researches point to a whole series of new problems; of these the most important are the following:—

(1) Reasoning from analogy, it may be supposed that the different modifications of boron and silicon will show, as regards specific heat, a behaviour similar to that of the modifications of carbon. This point I hope to settle by experiments carried out during the present winter.

(2) It may be supposed that the specific heats of those compounds into the composition of which carbon, silicon, or boron enters, will exhibit a variation with the temperature analogous to that exhibited by the elements themselves. My experiments, so far as they have gone, fully bear out the truth of this supposition.

The physical cause of the variation in the specific heat of carbon is to be sought for in the constitution of the atoms, not in that of the molecules.

On the supposition that the specific heats of the elements hydrogen and oxygen are as constant in their compounds as in the free state (and there seems no reason to doubt the truth of this supposition), it is possible, from a series of observations at different temperatures of the specific heat of a compound (C, H), (C, O), or (C, O, H), to deduce the specific heat of the carbon in the compound as a function of the temperature.

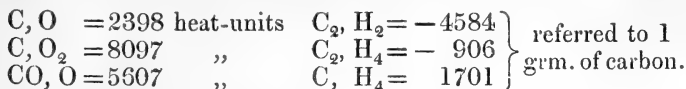
So far as my researches have gone, I find that, in gaseous and liquid carbon compounds, the specific heat of the carbon is a function of the temperature, but that the nature of this function varies from compound to compound. *The specific heat of carbon when in combination is a function of the temperature and of all those circumstances which influence the quality of the non-carbonated part of the compound molecule.* Thus the specific heat of carbon in carbon monoxide, CO, for every degree of temperature from  $-30^{\circ}$  to  $250^{\circ}$ , is totally different from the specific heat of carbon in the dioxide, CO<sub>2</sub>; the function of the temperature representing the specific heat of carbon in the compound CH<sub>4</sub> is of an entirely different nature from that representing the specific heat of the same element in the compound C<sub>10</sub>H<sub>16</sub>.

Hence it follows that the constitution of the carbon atom differs according to the nature of the molecule of which it forms a part; for example, the carbon in CO<sub>2</sub> is of a different nature from the carbon in CO. Hence it is self-evident that the "chemical value" of carbon is not constant; that "varying equivalency" or "polyequivalency" of carbon is possible, as is indeed exhibited in the compounds CO and CO<sub>2</sub>.

In the specific heat of carbon, considered as a function of the temperature, we have therefore a means of settling one of the most important questions in the theory of the carbon compounds—the question as to the constancy or variability of the nature of the carbon atom in the compounds formed by that element. A



number of facts connected with the heat of combination of carbon which have hitherto appeared anomalous seem to find their explanation in this variability of the carbon atom. Thus the heats of combination in certain reactions are as follows:—



On the assumption that the nature of the carbon atom does not vary, these facts are difficult of explanation. Regnault's results regarding the specific heats of liquid and gaseous carbon compounds\* are explained by adopting the hypothesis that the nature of the carbon atom varies in its different compounds. The great variations in the specific heats of the liquid carbon compounds observed by Regnault are due, not to the fact that these compounds are liquids, but to the immediate influence of the carbon atoms contained in these compounds. Hence all Regnault's endeavours to establish a relation between the varying specific heats of the liquids and their relative volumes must be fruitless. The unknown cause which Regnault admits, in the last words of his research, "on est obligé d'admettre qu'en outre des causes, telles que la dilatation, qui font certainement varier la capacité calorifique d'un même corps avec la température, il en existe d'autres, que nos moyens d'investigation ne sont pas parvenus jusqu'ici à définir," is to be found in the varying specific heat of the carbon atoms, which changes with the changes of temperature and of molecular constitution. Regnault, in his researches upon the specific heats of gaseous carbon compounds, gives merely the mean result for a certain temperature-interval, except in the case of carbon dioxide; from these mean results little can be deduced, if it be true that the specific heat is a function of the temperature, as in these cases the nature of this function is unknown. It is only from widely extended researches upon the specific heats of a number of gaseous and liquid carbon compounds that any deep insight can be obtained into the nature of carbon, and into the general laws regulating the specific heats of the compounds of this element. With this work I am now engaged; but some time must elapse ere my results are sufficiently advanced for publication; I have therefore summarized the points of interest, and showed the consequences which seem to follow from my researches, so far as these have been carried out.

(3) The question has yet to be answered, How, in reference to the atomic constitution of the elements carbon, boron, and silicon, can we on physical grounds harmonize all the foregoing results regarding the specific heats of these elements? Only

\* *Mém. de l'Acad de Paris*, vol. xxvi.

by assuming that the atom of these elements is not a simple but a complex structure built up of simpler elements. This hypothesis, put forward by Kopp, Berthelot, and others to account for the seeming exception of carbon &c. to Dulong and Petit's law, yet remains as the most probable means of accounting for the changes in the specific heats of those bodies, although it is now shown that they obey the above-named law. Before these questions regarding the constitution of the atoms of these elements can be answered, careful researches upon the specific heats of their compounds must be undertaken. I propose to discuss the theoretical bearings of these questions in another instalment of this paper.

Hohenheim, October 1874.

### XXXII. *On the Action of Solids in liberating Gas from Solution.*

By CHARLES TOMLINSON, F.R.S.\*

**I**F Fact and true Inference were friends and fellow-travellers, or if the latter followed the former at an easy distance, we should always find them on smooth roads and under a cloudless sky. Whoever discovered the one, would be quite sure that the other was close at hand, neither impeded by the quicksands of doubt, nor hidden from view by the fog of hypothesis. Mediocrity would then be as efficient as genius, and we should be constrained to acknowledge the truth of Lord Bacon's assertion, that "our method of discovering the sciences is such as to leave little to the acuteness and strength of wit, and indeed rather to level wit and intellect"†.

The difference between a non-scientific and a scientific intellect is supposed, at least in modern times, to consist in this, that while the one mixes up facts with their inferential ocular spectra in such a way as almost to justify the sarcasm that "there are more false facts than false theories current," the other carefully isolates facts from their theoretical or hypothetical shackles, and proclaims from the housetops "we *know* that these are facts, we *infer* that this is their explanation."

And with good reason; for a fact stands out in objective prominence, and, as such, must present the same aspect to every sane observer—whereas the inference is eminently subjective, taking its tone and texture from the mind of him who draws it, so that it is exposed to the warping influences of prejudice, of self-esteem which prefers its own theories to nature's truth, of

\* Communicated by the Author.

† "Nostra vero inveniendi scientias ea est ratio, ut non multum ingeniorum acumini et robori relinquatur; sed quæ ingenia et intellectus fere exæquet."—*Novum Organon*, lib. i. sect. lxi.

dyspepsia and other accidents. Hence two observers may draw entirely different inferences from the same fact, and both be equally wrong when the case comes to be referred to nature's high court of appeal.

When a scientific man says, "In the year 18— I established this fact," he is within philosophical bounds, supposing the fact to be such as can be repeated and verified by persons capable of performing an experiment with accuracy. But when he says, "In the year 18— I established this explanation," he becomes non-scientific, because he confuses that which admits of proof with that which can only be a matter of inference.

If, for example, I pour into a test-glass a quantity of soda-water and observe that numerous bubbles of gas cling to the side, and then pour soda-water into another test-glass that has just been made chemically clean, and find that no bubbles adhere to the side, I infer that chemical cleanliness in the latter case, and the absence of it in the former, are concerned in the phenomena. If a line be drawn within the clean glass by means of a glass rod smeared with grease or oil, such line becomes instantly covered with gas-bubbles. In such case it is fair to infer that a portion of the chemically clean surface is thus made unclean, and that the different behaviour of the gaseous solution depends on the distinction between chemically clean and chemically unclean.

But M. Gernez has recently informed us\* that in 1866 he established the conclusion that no gas is liberated below the surface of a supersaturated gaseous solution, such as Seltzer water, unless we introduce some kind of gaseous atmosphere, such as that which is retained on the surface of a solid body or in the capillary cavities of a porous body, and that it is into this atmosphere that the gas held in solution expands and escapes.

In 1867 I published in this Magazine† an account of a number of experiments in opposition to the view of M. Gernez, the object of which was to show that while a gaseous supersaturated solution, with its upper surface exposed to the air, gives off gas, either with effervescence or imperceptibly, the surface of the liquid confined by the sides of the vessel is subject to two modifications—(1) The state of chemical purity of their surface, and (2) the pressure exerted by them virtually on the liquid. (1) If the vessel be chemically clean, no gas is disengaged and no bubbles form on the sides, because the adhesion

\* *Comptes Rendus*, 4 Janvier 1875, p. 44. A translation of this Note is given in the *Phil. Mag.* for February last.

† "On the so-called 'Inactive' Condition of Solids," *Phil. Mag.* August and September, 1867.

between the sides and the gaseous solution is perfect; and therefore the sides may be regarded, *pro ratâ*, as merely a continuation of the liquid itself, and no bubbles will form there any more than in the central parts of the liquid. (2) But suppose the sides to be chemically unclean, adhesion is diminished or destroyed, and therefore the surface of the liquid next to such sides is virtually as free as its upper surface; consequently bubbles will form there, just as they do on the upper surface; only in the latter case they do not appear as bubbles (except during effervescence), because there is no pressure; the sides do exert pressure, and therefore bubbles are formed. Now it does not matter whether there be air or not between the sides and the liquid, since it is no function of air to induce the liberation of gas or the formation of gas-bubbles. It is really want of adhesion. A glass rod or other solid introduced into the liquid does nothing more than form new sides, as it were, to the vessel; and its effect is merely that of the sides. If chemically clean, the rod will form no bubbles around it, because the adhesion between it and the gaseous solution is perfect. If dirty, the adhesion is imperfect, and the surface of the liquid in contact with it will be as free, or almost so, as the upper surface.

I must refer to my paper for the experimental details; but I may be permitted to state briefly, that the various solids made chemically clean, or partly so, and plunged into soda-water, displayed no gas-bubbles except on the parts that had not been made clean—that a flint-stone was immediately covered with bubbles, but, broken into two parts, not a single bubble appeared on the newly fractured surfaces—that a rat's-tail file, properly cleaned, liberated no bubbles; so that I could not agree with M. Gernez that a solid, whatever its polish, "is covered with roughnesses that form a sort of network of capillary conduits, into which the surrounding gases penetrate and condense," that "the gas-bubbles thus imprisoned become the centres to which those that are dissolved pass."

But M. Gernez says that if a small cavity be worked into the end of a glass rod, and this, full of air, be lowered into a gaseous solution, the gas escapes into it in bubbles. I submerged a cage of fine wire gauze in soda-water, but there was no escape of gas so long as it was chemically clean. When taken out, rolled between the slightly greased hands, and again lowered into the soda-water, the gas escaped from its side in bubbles with an audible noise.

Now it cannot be maintained that contact between the cage and the hands imparted to the cage a film of air instead of a film of oil—or that a slightly greasy rod introduced into a chemically clean glass containing soda-water, and rubbed against

the side, below the surface, introduces air and not oil—or that a clean glass rod on which no bubbles appear, taken out and drawn with friction through the hand, acquires an air coating, which causes it to be covered with bubbles when returned to the soda-water. A man must be strangely fascinated with his own hypothesis to maintain such a proposition; and yet M. Gernez, after a lapse of eight years, attempts to explain my results (which have been confirmed by Professor Schrötter\*) by seriously maintaining that the effect of washing with caustic potash solution, boiling distilled water, or alcohol is not to make the solid surfaces chemically clean, but to deprive them of the film of air which clings to them. I quote his language:—"Si l'on a soin de dissoudre, par des lavages successifs à la potasse, à l'eau distillée bouillante et à l'alcool, la couche superficielle des vases de verre en certains points de laquelle se trouverait retenue une petite quantité d'air, on constate qu'il ne se forme plus une seule bulle gazeuse sur la paroi baignée par le liquide, pas plus qu'à l'intérieur de la solution sursaturée entre des limites de température et de pression très-étendues" (p. 44).

As to the action of porous bodies in liberating gas from solution, I have long since endeavoured to show that they act by reason of that strong adhesive force of which the absorptive power of charcoal for various gases affords striking examples. Charcoal, or other porous body, in a boiling liquid (which I have defined as a supersaturated solution of its own vapour †) powerfully absorbs the vapour of that liquid, but cannot retain it so long as the liquid is maintained at or near its boiling-point; hence it is constantly pouring forth streams of vapour, and by its presence so far facilitates the escape of vapour, that in distillations from 20 to 30 per cent. more liquid is condensed in consequence of the presence of a few bits of charcoal, while at the same time *soubresauts* are prevented.

It appears to me that porous bodies liberate gas from gaseous supersaturated solutions by virtue of that same force of adhesion by which gases become imprisoned in charcoal &c. A piece of cocoanut-shell charcoal, for example, in soda-water, condenses a certain amount of carbonic acid within its pores; and the adhesive force continues active even though a further supply of gas can find no entrance. In seeking to enter, it becomes disengaged from the water, and rises in a stream apparently from the surface of the charcoal. Under diminished pressure the gas escapes in large quantities from the charcoal itself, while the adhesive force is restored with the pressure.

\* Pogg. Ann. vol. cxxxvii.

† Proceedings of the Royal Society, January 21, 1869.

It was stated by De Luc\* that water purged of air cannot be boiled; and Donny† gives an experiment in which water, heated in an oil-bath many degrees above its boiling-point, at length suddenly bursts into steam with the force of an explosion. The water, it is said, cannot boil unless air be present in the liquid, because, according to De Luc's theory, or, as it is now called, the theory of Clausius, air is required for the steam to expand into. There is a well-known experiment by Grove, in which water covered with a layer of oil was repeatedly boiled, and it was found impossible to get rid of the dissolved air. I repeated this experiment some years ago, and found that air was carried down by the oil itself. As soon as the water was fairly boiling, the oil was broken up into globules, and one or more bubbles of air attached to the oil was carried down into the liquid. On removing the lamp, the oil rose to the surface with a ring of air-bubbles beneath. But supposing all these facts to be accurately represented, and that a liquid, at or near the boiling-point, is constituted like soda- or Seltzer-water, then I cannot admit that a solid, such as a glass rod, introduced into a boiling liquid (water for example), becomes covered with bubbles of steam by virtue of the air carried down by the rod. If the rod be unclean‡ (that is, contaminated with a greasy film), the steam-bubbles cover it precisely after the manner of the gas-bubbles, because there is adhesion between the steam-bubbles and the film and not between the water and the film, and hence there is a separation. A chemically clean glass rod has no such action, not because the act of cleaning it deprives it of its adhering air, but because there is perfect adhesion between a vaporous supersaturated solution and a chemically clean surface.

It is perhaps a fortunate thing for science (the object of which, some people suppose, is the discovery of truth) that men are so enamoured of their own theories that they defend them with the strongest dialectical weapons that they can furbish up; and it is out of the battle of rival theorists that truth finally emerges. So that while each man pursues science with perfect honesty and sincerity, but nevertheless for his own glory, Nature, like one of her own stars, *ohne Hast aber ohne Rast*,

\* "Quand on a préalablement purgé l'eau de tout l'air qu'elle contenoit, elle ne peut plus bouillir; et la raison en est que les vapeurs ne peuvent se former qu'à des surfaces libres."—*Recherches* &c., Geneva, 1772. For authorities on some interesting points in connexion with boiling, see "Historical Notes" &c., Phil. Mag. for March 1869.

† *Mém. de l'Acad. Roy. de Bruxelles*, vol. xvii. 1845.

‡ In a paper contained in the Phil. Mag. for October 1868, a precise meaning is given to the terms "clean" and "unclean." See also Phil. Mag. for April 1873 and November 1874.

moves silently on, and at length asserts herself, with perfect indifference to the fame of her votaries, and the final verdict is in favour of truth. Many a fact wanders about the world as a scientific waif, not finding rest in any sufficient theory, until at length it falls into its proper place and becomes associated with a host of other facts, outcasts like itself, or interlopers in theoretical lodging-houses; but now, in its right place, it performs valuable and unexpected work. The motions of camphor &c. on water were known during upwards of a century and a half before they found their true resting-place in the surface-tension of liquids; and it is quite possible that the varied phenomena connected with supersaturation may, at some future time, be embraced by some general law, or be held together by some satisfactory theory, when the labours of those who have been working on the subject from the commencement of this century to the present time will have been forgotten, or referred to by the curious in journals that will then have become old, with a wondering smile that men could have been so blind to the obvious teaching of the facts.

Highgate, N. March 9, 1875.

XXXIII. *Note on Partitions.* By J. W. L. GLAISHER, M.A.\*

**D**ENOTING by  $P(a, b, c \dots q)x$  the number of ways of forming  $x$  by addition of the elements  $a, b, c \dots q$ , each element being repeatable any number of times, I propose to consider the value of  $P(1, 3, 5 \dots)x$ , viz. the number of ways of partitioning  $x$  into parts all of which shall be uneven.

To fix the ideas, suppose  $x=10$ , and consider any one partition, say  $1+1+3+5$ ; write this in the form

$$\begin{array}{cccc} 1, & 1, & 1, & 1 \\ & & 2, & 4, \end{array}$$

the top line consisting of units only (as many as the partition contains parts), and the second line containing only even numbers; the other partitions of 10 into four parts, viz.  $1+1+1+7$ ,  $1+3+3+3$  are to be written

$$\begin{array}{cccc} 1, & 1, & 1, & 1 & 1, & 1, & 1, & 1 \\ & & 6, & & 2, & 2, & 2, & ; \end{array}$$

so that the number of partitions of 10 into four uneven parts is equal to the number of partitions of  $10-4$  into even parts not exceeding four in number. It is at once evident that this process is general, and that the number of partitions of  $2x$  into  $2r$  uneven parts is equal to the number of ways of partitioning

\* Communicated by the Author.

$2x-2r$  into even parts, subject to the condition that the number of these latter (even) parts must not exceed  $2r$  (the number of units in the top line). Thus, writing for the moment  $P'_n(a, b, c, \dots)$  to represent the number of ways of partitioning  $x$  into the parts  $a, b, c, \dots$ , no more than  $n$  of such parts appearing in any one partition, we see that

$$P(1, 3, 5 \dots)2x = 1 + P'_2(2, 4, 6 \dots)(2x-2) \\ + P'_4(2, 4, 6 \dots)(2x-4) \dots + P'_{2x-2}(2, 4, 6 \dots)2,$$

the first term in the latter expression corresponding to the single partition of  $2x$  as the sum of  $2x$  units. Now obviously the number of ways of partitioning  $2n$  into the parts  $2, 4, 6 \dots$  is equal to the number of ways of partitioning  $n$  into the parts  $1, 2, 3 \dots$ , so that

$$P(1, 3, 5 \dots)2x = 1 + P'_2(1, 2, 3 \dots)(x-1) \\ + P'_4(1, 2, 3 \dots)(x-2) \dots + P'_{2x-2}(1, 2, 3 \dots)1,$$

which, transformed by means of the well-known theorem

$$P'_n(1, 2, 3 \dots)x = P(1, 2, 3 \dots n)x, \quad \dots \dots (1)$$

becomes

$$P(1, 3, 5 \dots)2x = 1 + P(1, 2)(x-1) + P(1, 2, 3, 4)(x-2) \dots \\ + P(1, 2 \dots 2x-2)1. \quad \dots \dots (2)$$

By a similar method we easily arrive at the expression for the decomposition of an uneven number, viz.

$$P(1, 3, 5 \dots)(2x+1) = 2 + P(1, 2, 3)(x-1) \\ + P(1, 2, 3, 4, 5)(x-2) \dots + P(1, 2, 3 \dots 2x-1)1, \quad (3)$$

formulæ expressing the value of  $P(1, 3, 5 \dots)x$  in terms of partitions into the elements  $1, 2; 1, 2, 3, \&c.$ , and which have thus been obtained by general reasoning without analysis: they can, of course, be derived more directly by means of the identity

$$\frac{1}{1-x \cdot 1-x^3 \cdot 1-x^5 \dots} = 1 + \frac{x}{1-x^2} + \frac{x^2}{1-x^2 \cdot 1-x^4} \\ + \frac{x^3}{1-x^2 \cdot 1-x^4 \cdot 1-x^6} + \&c.$$

The proposition (1) that has been used (viz. that the number of partitions of  $x$  into parts not exceeding  $n$  in number is equal to the number of partitions of  $x$  into the parts  $1, 2, 3 \dots n$ ) admits of almost intuitive proof by Mr. Ferrers's method of breaking up and arranging the parts in a partition, so that when read as lines we obtain the number of partitions into parts not exceeding  $n$  in number, and when read as columns the number of partitions into  $1, 2, 3 \dots n$ : see *Phil. Mag. S. 4. vol. v. p. 201 (1853)*.



An application of the same principle affords another transformation of some interest for  $P(1, 3, 5 \dots)x$ . It was proved by Euler that  $P(1, 3, 5 \dots)x$  is equal to the number of partitions of  $x$  into the parts 1, 2, 3... in which each part only appears once in each partition, or, say, is equal to  $P(1, 2, 3 \dots)x$  without repetitions. Now, applying Mr. Ferrers's method to the latter, we see that a partition without repetitions corresponds to a partition without omissions. For example, writing  $1+2+3+5$  as

$$\begin{array}{c} 1 \\ 1, 1 \\ 1, 1, 1 \\ 1, 1, 1, 1, 1 \end{array}$$

and adding the columns, we obtain  $1+1+2+3+4$ ; and it is clear that though any part may appear any number of times, on part can appear unless all the lesser parts appear also. We thus see that

$$P(1, 3, 5 \dots)x = P(1, 2, 3 \dots)x \text{ without omissions ;}$$

and this latter quantity is equal to

$$\begin{aligned} &1 + P(1, 2)(x-1-2) + P(1, 2, 3)(x-1-2-3) \\ &+ P(1, 2, 3, 4)(x-1-2-3-4) + \&c.; \quad (4) \end{aligned}$$

for the second term represents the number of partitions of  $x$  into parts in which both 1 and 2 must occur and no higher part can occur; the third term represents the number of partitions in which 1, 2, 3 must, and no higher part can, occur, &c. By use of the well-known theorem

$P(1, 2, 3 \dots n)(x-n) + P(1, 2, 3 \dots n-1)x = P(1, 2, 3 \dots n)x$  (which can be readily established by general reasoning), the last equality can be transformed into

$$\begin{aligned} &P(1, 3, 5 \dots)x = P(1, 2)(x-1) \\ &+ P(1, 2, 3, 4)(x-1-2-3) + \&c., \quad (5) \end{aligned}$$

which can be at once identified with the formula

$$\begin{aligned} 1 + x \cdot 1 + x^2 \cdot 1 + x^3 \dots &= 1 + \frac{x^1}{1-x \cdot 1-x^2} \\ &+ \frac{x^{1+2+3}}{1-x \cdot 1-x^2 \cdot 1-x^3 \cdot 1-x^4} + \&c. \end{aligned}$$

That Mr. Ferrers's method should, as it were, afford a demonstration of this identity is what we should expect, as it was in effect remarked by Mr. Sylvester (Brit. Assoc. Report, 1871, p. 25, Sect. Proc.) that it established Euler's more general

identity

$$1 + xz \cdot 1 + x^2z \cdot 1 + x^3z \dots = 1 + \frac{xz}{1-x} + \frac{x^3z^2}{1-x \cdot 1-x^2} + \&c.$$

The value of  $P(1, 3, 5 \dots)x$  given by (4) is in fact that found by Euler (*Opera minora collecta*, vol. i. p. 93). The class of partitions without omissions is one which has not, I believe, been particularly noticed before; and it is curious that it should be identical with the partitionment into uneven numbers.

There is also another mode of transforming this latter class of partitions, which can be best made clear by an example. Thus, consider the partition  $1 + 3 + 3 + 7$ , and arrange the parts as in the following scheme:—

1	1	1	1
			1
2	2		1
1	2		1

the 1 occupying the left-hand lower corner, the three squares surrounding it being occupied by 2's, as there are two 3's in the partition, the next five squares being left vacant as there is no 5, and the next seven squares being filled by 1's as there is one 7. Then dividing the square into similar belts to those which represented the different parts in its formation, only beginning at the opposite (viz. the upper right-hand) corner, we have the parts 1, 1+1, 1+2+1, 1+2+1+2+1, that is 1, 2, 4, 7, which are always thus given in order of magnitude, and are subject to the following laws of formation, viz. :—that any number of parts (except the first) may be equal; but that, taking no account of these repetitions, *i. e.* regarding, for example,  $a + b + b + c$  simply as  $a + b + c$ , then the parts  $a, b, c, d$ , &c. are such that  $b = 2a + \alpha$ ,  $c = b + \alpha + \beta$ ,  $d = c + \beta + \gamma$ , &c. (so that the second part must be at least the double of the first). The same decomposition may also be derived without a diagram by observing that, for example,  $a + 3b + 7d = d + (2d) + (2d + b) + (2d + 2b + a)$ ; but the mode of formation is too complicated to render the transformation one of much interest.

The number of transformations of  $P(1, 3, 5 \dots)x$ , however, is noteworthy, as we have seen the equivalence of the numbers of (i) partitions into the uneven elements 1, 3, 5 ..., repetitions not excluded; (ii) partitions into the elements 1, 2, 3 ... without repetitions; (iii) partitions into the parts

1, 2, 3 . . . without omissions; (iv) partitions into the elements 1, 2, 3 . . . in which each must appear twice at least, except the largest part, which need only appear once, but may appear any number of times; (v) the partitions described in the last paragraph.

Taking Euler's example of  $x=10$ , omitting for brevity the signs connecting the parts, and writing, *ex. gr.*,  $1+1+2+2+4$  as  $1^2 2^2 4$ , the partitions of the different kinds are for (i)  $1^{10}$ ,  $1^7 3$ ,  $1^5 5$ ,  $1^3 7$ ,  $19$ ,  $13^3$ ,  $1^4 3^2$ ,  $1^2 3 5$ ,  $37$ ,  $5^2$ ; for (ii)  $10$ ,  $19$ ,  $28$ ,  $37$ ,  $46$ ,  $127$ ,  $136$ ,  $145$ ,  $235$ ,  $1234$ ; for (iii)  $1^{10}$ ,  $1^8 2$ ,  $1^6 2^2$ ,  $1^4 2^3$ ,  $1^2 2^4$ ,  $1^3 2 3$ ,  $1^2 2^2 3$ ,  $12^3 3$ ,  $1234$ ; for (iv)  $10$ ,  $1^2 8$ ,  $1^4 6$ ,  $1^6 4$ ,  $1^8 2$ ,  $3^2 4$ ,  $2^2 6$ ,  $1^2 2^2 4$ ,  $1^4 2^3$ ,  $2^5$ ; for (v)  $10$ ,  $19$ ,  $127$ ,  $12^2 5$ ,  $12^3 3$ ,  $37$ ,  $28$ ,  $136$ ,  $1234$ ,  $24^2$ .

Putting  $x=10$  in (3), we have

$1 + P(1, 2)4 + P(1, \dots 4)3 + P(1, \dots 6)2 + 1 = 1 + 3 + 3 + 2 + 1$ ; while (5) gives  $P(1, 2)9 + P(1, 2, 3, 4)4 = 5 + 5$ . There is a formula implicitly given by Euler (*Opera minora collecta*, vol. i. p. 93) which may be noticed here for the sake of completeness, viz.

$$P(1, 3, 5 \dots)x = P(1, 2, 3 \dots)x - P(1, 2, 3 \dots)(x-2)$$

$$- P(1, 2, 3 \dots)(x-4) + P(1, 2, 3 \dots)(x-10) + \&c.,$$

the terms being after the first alternately negative and positive in pairs, and the general term being  $P(1, 2, 3 \dots)(x-3n^2+3n)$ . This formula would, of course, be quite inappropriate for the calculation of  $P(1, 3, 5 \dots x)$ ; for  $x=10$  it gives

$$42 - 22 - 11 + 1 = 10.$$

Cambridge, March 10, 1875.

#### XXXIV. On the Work that may be gained during the Mixing of Gases. By LORD RAYLEIGH, M.A., F.R.S.\*

THE well-known fact that hydrogen tends to escape through fine apertures more rapidly than air enters to supply its place, even although the advantage of the greater pressure may be on the side of the air, proves that the operation of mixing the two gases has a certain mechanical value. In a common form of the experiment a tube containing hydrogen and closed at the upper end with a porous plug of plaster of Paris stands over water. In a short time the escape of hydrogen creates a partial vacuum in the tube, and the water rises accordingly. Whenever then two gases are allowed to mix without the performance of work, there is dissipation of energy, and an opportunity of doing work at the expense of low temperature heat has been for ever lost. The present paper is an attempt to calculate this amount of work.

\* Communicated by the Author.

The result at which I have arrived is extremely simple. It appears that the work that may be done during the mixing of the volumes  $v_1$  and  $v_2$  of two different gases is the same as that which would be gained during the expansion of the first gas from volume  $v_1$  to volume  $v_1 + v_2$ , together with the work gained during the expansion of the second gas from  $v_2$  to  $v_1 + v_2$ , the expansions being supposed to be made into vacuum. Now these expansions may be considered actually to take place; and thus the rule is brought under Dalton's principle that each gas behaves to the other as a vacuum. It is understood that the gases follow the common law of independent pressures, so that the total pressure is always the sum of those which would be exerted by each gas in the absence of the other.

We will take first the case when one gas is condensable, and estimate how much work must be done in order to separate the components of a mixture. Suppose, then, that a long cylinder, closed at the bottom, contains a uniform mixture of (for example) hydrogen and steam confined under a piston, and that the walls of the cylinder are maintained at a constant temperature. When the piston descends, heat will be generated; but the operation is supposed to proceed so slowly, that not only is the temperature rigorously constant throughout, but also the mixture is at any time in that condition which it would finally attain were the descent of the piston arrested. The pressure on the piston resisting the descent is by hypothesis the sum of those which it would experience from the hydrogen and steam separately\*. When the space under the piston is reduced to that which the given quantity of steam is capable of saturating at the given temperature, condensation commences and continues as the steam-space is gradually diminished.

By carrying this process sufficiently far, the condensation of the steam may be effected with any desired degree of completeness, and thus the water and hydrogen separated. A second movable piston may now be inserted immediately over the condensed water, and a very gradual expansion allowed until the original total volume is recovered. If the second piston be allowed free motion, the constituents of the original mixture are now separated, under equal pressures, and occupying the same total volume as before; and the question is, how much work has been expended in arriving at this state of things?

In view of the fact that during the first part of the operation the hydrogen and steam press independently, it is clear that the total work done is the same as that which would be required to

\* For the sake of simplicity we may suppose a vacuum on the other side of the piston, though, of course, any constant pressure would give finally no result.

compress the hydrogen from the original volume  $v_1 + v_2$  to the volume  $v_1$  if no steam were present, together with the work necessary to compress the steam from  $v_1 + v_2$  to  $v_2$  if no hydrogen were present. And since every step of this process is reversible, the same amount of work might be gained in making the mixture, and is dissipated if the mixture is allowed to take place by free diffusion.

The same argument will apply when the condensation of one of the gases is effected by chemical means. Suppose, for example, that we have a mixture of carbonic anhydride and hydrogen at a red heat, and that it is proposed to absorb the carbonic gas with quicklime. It has been proved by Debray that at every temperature above a certain point carbonic gas in contact with quicklime and carbonate has a definite tension; any excess will be absorbed by the lime, and any deficiency supplied by a decomposition of the carbonate.

If the tension of the carbonic gas in the given mixture be higher than that proper to the temperature, absorption will take place in an irreversible manner. In order to prevent dissipation, the mixture of gases must be first expanded until the tension of the carbonic gas is no higher than that corresponding to the temperature at which it is proposed to work. When the contact is made, the mixture may be very slowly condensed, so that after the point is passed at which chemical action commences, the tension of the carbonic anhydride remains constant. This process may be continued until nearly all the carbonic anhydride is absorbed. The hydrogen may then be separated. The space over the carbonate of lime must next be slowly increased until the original quantity of carbonic gas has been again evolved, when the connexion with the quicklime must be cut off. It now only remains to reduce the separated gases to the same pressure and to a total volume equal to that of the original mixture.

From the preceding considerations we may, I think, infer that the law above stated is general whenever the gases really press independently; for it is difficult to see how its truth could depend on what would seem to be the accident of the existence or non-existence of a chemical capable of absorbing one or other of the gases.

It is worthy of notice that exactly the same rule applies for the mechanical value of the separation of two gases, even when the pressures are different; for we get the same result whether we first before mixing allow the pressures to become equal and add the work gained in this process to that due to the subsequent mixing, or whether we calculate at once the work due to the separate expansion of the two gases from their original volumes to the total volume of the mixture.

In like manner the work that can be gained during the mixing of any number of pure and different gases, which press independently, is the sum of those due to the expansions of the several gases from their original to their final volumes, where the volume of a gas is understood to mean the space in which the gas is confined.

The next problem which presents itself is that of finding the work that may be done during the mixture of two quantities of mixed gases—for example, oxygen and hydrogen. Suppose the two mixtures to be contained in a cylinder, and separated from one another by a piston which moves freely. The rule is that the work required to be estimated is that which would be gained during the equalization of the oxygen-pressures if the hydrogen were annihilated, together with that which would be gained during the equalization of the hydrogen-pressures if the oxygen were annihilated.

If the proportions of the gases are the same in the two mixtures, and also the total pressures, there is, of course, no possibility of doing work. If, on the other hand, the gas on the one side of the piston be pure oxygen, and on the other side pure hydrogen, the more general rule reduces to that already given for pure gases.

I now pass to another proof of the fundamental rule, depending on the possibility of separating two gases of different densities by means of gravity. In a vertical column maintained at a uniform temperature, two gases which press independently will arrange themselves each as if the other were absent. Consequently, if there be any difference in density, the percentage composition will vary at different heights, and a partial separation of the gases is thus effected.

Imagine now a large reservoir containing gas at sensibly constant pressure, on which is mounted a tall narrow vertical tube; and first, in order to understand the operation more easily, let there be only one kind of gas present. If  $p$  be the pressure and  $\rho$  the density,  $p = k\rho$ , since the temperature is constant; and if  $z$  be the height measured from the reservoir in which the pressure is  $P$ ,

$$dp = -g\rho dz = -\mu p dz, \text{ if } \mu = g/k;$$

whence, by integration,

$$p = P e^{-\mu z} \dots \dots \dots (1)$$

expresses the law of variation of pressure with height. Suppose now that a small quantity of gas of volume  $v$  is (1) removed from the top of the tube, (2) compressed to volume  $v_0$  until it is of the same pressure as the gas in the reservoir, (3) allowed to fall through the height  $z$  to the level of the reservoir, and (4) forced

into the reservoir. The effect of this series of operations is *nil*, and there can be neither gain nor loss of work. The work gained in the first operation is consumed in the fourth, since  $pv = Pv_0$ , so that attention may be confined to the second and third operations. Now the work consumed in the compression from  $v$  to  $v_0$  is

$$\int_{v_0}^v p dv = Pv_0 \int_{v_0}^v \frac{dv}{v} = Pv_0 \log \frac{v}{v_0} = Pv_0 \log \frac{P}{p}; \quad \dots \quad (2)$$

and the work gained in the descent

$$= gz\rho_0 v_0 = \mu z v_0 P.$$

And these are equal, since

$$\log \frac{P}{p} = \mu z;$$

so that on the whole no work is lost or gained.

The case is different when there are two kinds of gases present. Although, as before, the work gained in the first operation is consumed in the fourth, there is no longer compensation in the second and third operations. If  $P_1$  and  $P_2$  are the partial pressures in the reservoir, the work required for the compression from  $v$  to  $v_0$  is

$$(P_1 + P_2)v_0 \log \frac{v}{v_0}.$$

On the other hand, the work gained in the descent is

$$gzv_0 \left( \frac{Q_1}{k_1} + \frac{Q_2}{k_2} \right) = zv_0 (\mu_1 Q_1 + \mu_2 Q_2),$$

if  $Q_1, Q_2$  are the partial pressures of the abstracted gas after condensation to volume  $v_0$ . Thus, on the whole, if  $W$  be the work done on the gases, since  $Q_1 + Q_2 = P_1 + P_2$ ,

$$\frac{W}{v_0} = Q_1 \left( \log \frac{v}{v_0} - \mu_1 z \right) + Q_2 \left( \log \frac{v}{v_0} - \mu_2 z \right).$$

Now  $p_1 = P_1 \epsilon^{-\mu_1 z}$ , and  $vp_1 = v_0 Q_1$ ; so that

$$vP_1 \epsilon^{-\mu_1 z} = v_0 Q_1.$$

Accordingly

$$\log \frac{v}{v_0} - \mu_1 z = \log \left( \frac{Q_1}{P_1} \epsilon^{+\mu_1 z} \right) - \mu_1 z = \log \frac{Q_1}{P_1}.$$

Similarly

$$\log \frac{v}{v_0} - \mu_2 z = \log \frac{Q_2}{P_2};$$

and thus

$$W = v_0 \left\{ Q_1 \log \frac{Q_1}{P_1} + Q_2 \log \frac{Q_2}{P_2} \right\} \dots \dots \dots (3)$$

Since the process is reversible, (3) gives the work which may be done during the mixing of a volume  $v_0$  of two gases under the partial pressures  $Q_1$  and  $Q_2$ , with a large quantity of the same gases under an equal total pressure, but with partial pressures  $P_1$  and  $P_2$ .

The quantity denoted by  $W$  can never be negative. To verify this from (3), write it in the form

$$-\frac{W}{v_0(P_1+P_2)} = x' \log \frac{x}{x'} + y' \log \frac{y}{y'} = \log \left\{ \left( \frac{x}{x'} \right)^{x'} \left( \frac{y}{y'} \right)^{y'} \right\}, \quad (4)$$

where

$$x = \frac{P_1}{P_1+P_2}, \quad y = \frac{P_2}{P_1+P_2}, \quad x' = \frac{Q_1}{Q_1+Q_2}, \quad y' = \frac{Q_2}{Q_1+Q_2};$$

so that  $x+y=x'+y'=1$ .

Now (Todhunter's 'Algebra,' p. 392) if  $a, b, c, \dots$  be any positive quantities,

$$\frac{a+b+c+d+\dots}{n} > (abcd\dots)^{\frac{1}{n}}.$$

Suppose that  $a, b, c, \dots$  consist of  $p$  equal quantities  $\alpha$  and  $q$  equal quantities  $\beta$ ; then

$$\frac{p}{n}\alpha + \frac{q}{n}\beta > \alpha^{\frac{p}{n}}\beta^{\frac{q}{n}}.$$

If now we take

$$\frac{p}{n} = x', \quad \frac{q}{n} = y', \quad \alpha = \frac{x}{x'}, \quad \beta = \frac{y}{y'},$$

we see that

$$x+y > \left( \frac{x}{x'} \right)^{x'} \left( \frac{y}{y'} \right)^{y'},$$

and therefore, since  $x+y=1$ , that  $W$  is always positive, unless  $\alpha=\beta$ , in which case the composition of the two mixtures is the same, and  $W$  vanishes.

We have now to show how the formula for the mixture of two pure gases may be derived from (3). Let  $v_1$  be the volume of the first gas and  $v_2$  of the second, at the constant pressure  $P_1+P_2$ . The value of the interdiffusion of  $v_1$  and  $v_2$  must be the same as that of their diffusion into a large quantity of a mixture whose composition is identical with that of the mixture of  $v_1$  and  $v_2$ . For, on this supposition, the separation of the two mixtures spoken of would have no mechanical value. Now by (3) the value of  $W$  for the diffusion of a quantity  $v_0$  of pure gas into a large quantity of a mixture whose partial pressures are  $P_1$



and  $P_2$  is (since  $Q_2$  and  $Q_2 \log Q_2$  vanish)

$$W = (P_1 + P_2)v_0 \log \frac{P_1 + P_2}{P_1}; \quad . \quad . \quad . \quad (5)$$

and hence the value of  $W$  for the interdiffusion of the quantities  $v_1$  and  $v_2$  is

$$W = v_1(P_1 + P_2) \log \frac{P_1 + P_2}{P_1} + v_2(P_1 + P_2) \log \frac{P_1 + P_2}{P_2},$$

or, since by hypothesis

$$P_2 : P_1 = v_2 : v_1,$$

$$\begin{aligned} W &= (P_1 + P_2) \left\{ v_1 \log \frac{v_1 + v_2}{v_1} + v_2 \log \frac{v_1 + v_2}{v_2} \right\} \\ &= (P_1 + P_2) \log \frac{(v_1 + v_2)^{v_1 + v_2}}{v_1^{v_1} v_2^{v_2}}. \quad . \quad . \quad . \quad (6) \end{aligned}$$

This equation agrees with the rule enunciated at the beginning of this paper, inasmuch as  $(P_1 + P_2)v_1 \log \frac{v_1 + v_2}{v_1}$  represents the work gained in the expansion of the first gas from volume  $v_1$  to volume  $v_1 + v_2$ , and  $(P_1 + P_2)v_2 \log \frac{v_1 + v_2}{v_2}$  represents the corresponding quantity for the second gas.

The significance of equation (5) may perhaps be more fully brought out by the following investigation of it. Whatever the relative proportions of the two gases in the reservoir may be, it will always be possible by going high enough to obtain a small quantity of the lighter gas in any required degree of purity. The removal of this at the top of the tube, its condensation to the pressure in the reservoir, the fall to the level of the reservoir, and the introduction into the reservoir would, on the whole, require no work to be done if this kind of gas had alone been present. The only effect of the heavier gas is to render necessary a greater condensation in the third operation; and thus  $W$  is the work that is required to condense the gas from the partial pressure  $P_1$  to the total pressure in the reservoir  $P_1 + P_2$ , whence equation (5) follows at once. If it is desired to isolate a small quantity of the heavier gas, the tube must be taken downwards.

It is to be observed that the work required to force a given quantity of gas into a large reservoir containing gas at the same pressure is independent of this pressure, since, according to Boyle's law,  $v$  is diminished in the same proportion that  $p$  is increased.

The principle of dissipation may be employed to prove that the pressure in a vertical column of mixed gases is greater

when there is free diffusion than when the gases are uniformly mixed; for if the gases be allowed to rise from the reservoir tolerably quickly (or if a series of movable pistons be interpolated), the composition in the tube will be the same as in the reservoir. If free diffusion be now allowed, there must be dissipation. The original state of things will be restored if the mixture be slowly forced back into the reservoir; and accordingly the work consumed in condensation must be greater than that gained in the expansion. In fact it may be proved algebraically by a process somewhat similar to that applied to equation (3), that the pressure of the gases under free diffusion  $p$ , where

$$p = P_1 e^{-\mu_1 z} + P_2 e^{-\mu_2 z}, \quad \dots \quad (7)$$

is greater than the pressure of a uniform mixture  $p'$ , where

$$p' = (P_1 + P_2) e^{-z \frac{\mu_1 P_1 + \mu_2 P_2}{P_1 + P_2}} \quad \dots \quad (8)$$

It is, however, possible to imagine other distributions which shall give a pressure greater than (7). The mechanical equilibrium gives one equation involving the two quantities  $p_1$  and  $p_2$ , viz.

$$\frac{dp_1}{dz} + \frac{dp_2}{dz} + \mu_1 p_1 + \mu_2 p_2 = 0; \quad \dots \quad (9)$$

and the subsidiary conditions are that  $p_1 = P_1$ ,  $p_2 = P_2$ , when  $z = 0$ . Hence we may take as the most general solution,

$$p_1 = P_1 e^{-\mu_1 z} + e^{-\mu_1 z} \int_0^z e^{\mu_1 x} X dx,$$

$$p_2 = P_2 e^{-\mu_2 z} - e^{-\mu_2 z} \int_0^z e^{\mu_2 x} X dx,$$

where  $X$  is an arbitrary function of  $x$ . Thus the total pressure

$$p_1 + p_2 = P_1 e^{-\mu_1 z} + P_2 e^{-\mu_2 z} + \int_0^z \{e^{-\mu_1(z-x)} - e^{-\mu_2(z-x)}\} X dx. \quad \dots \quad (10)$$

For free diffusion  $X=0$ ; but it could always be taken so as to make the integral either positive or negative, as might be desired.

The work required to decompose a mixture of gases is in general small, and could scarcely be of much importance from an industrial point of view. When, however, the proportion of one ingredient is very insignificant, more work is required. Thus the separation of the carbonic anhydride from the atmosphere would require, relatively to the quantity obtained, a much larger expenditure of work than the separation of the oxygen. This

consideration shows that extreme purity in any gas will always be attained and maintained with difficulty. Even when the necessary work is small, as in the separation of oxygen from the atmosphere, it is well to bear in mind that some work is absolutely essential. The reversible absorption of the oxygen of air may be effected by a substance like baryta; but we must not expect to recover the pure oxygen at the same temperature and under a pressure equal to the total pressure at which it was absorbed. Either the temperature must be raised, or the gas must be exhausted at a pressure less than that under which it existed in the mixture during the absorption. It is just possible that this point might be found to be of practical importance in the solution of the problem of extracting oxygen from the air.

XXXV. *Notices respecting New Books.*

*An Elementary Treatise on the Integral Calculus, containing Applications to Plane Curves and Surfaces, with numerous Examples.* By BENJAMIN WILLIAMSON, A.M., Fellow and Tutor, Trinity College, Dublin. London: Longmans, Green, and Co. 1875 (crown 8vo, pp. 267).

WE have already noticed Mr. Williamson's 'Elementary Treatise on the Differential Calculus' (vol. xliii. p. 307), and have now to perform the same office for his companion volume on the Integral Calculus,—a work characterized by the same excellences as those which marked the previous volume. It is written with clearness and accuracy, and is illustrated with an abundance of examples. Its contents may be briefly described as consisting of three parts. In the first are given the ordinary methods of integration, viz. by reduction to known forms, of rational fractions, by successive reduction, and by rationalization. In this part of the work, which occupies the first five chapters, integration is treated simply as the inverse of the process of differentiation. In the next part, the sixth chapter, a sufficient account is given of Definite Integrals; and here the student is introduced to the notion of integration as a process of summation. In the latter part of this chapter some account is given of the Eulerian Integrals, particularly of the second; and at the end there is a table of values of the gamma function ( $\log \Gamma(p) + 10$ ) from  $p=1.000$  to  $p=1.999$  to six places of decimals; but the method of constructing this table is omitted as "too complicated for insertion in an elementary treatise." The third part of the book, comprised in chapters seventh, eighth, and ninth, explains the application of the Integral Calculus to finding areas and lengths of curves and volumes of solids. In this part will be found many useful and interesting properties of curves; *e. g.* in addition to those which we might expect to find almost as a matter of course, we may mention Lambert's theorem on the area of an

elliptic sector, areas of roulettes, the theory of Amsler's planimeter, Landen's theorem on the length of a hyperbolic arc, Steiner's theorem on the rectification of roulettes, and some others.

It will be seen, from this brief account of the contents, that the work is of a strictly elementary character. Such subjects as the expansion of functions in trigonometrical series, elliptic functions, and the Calculus of Variations are simply omitted; while the transformation of the independent variable and double integration are but briefly noticed. Within the limits which the author has assigned to himself, however, the treatment is very full and satisfactory; and the work is well adapted to the wants of those for whom it is written, viz. students in the Universities, very few of whom (as we suppose) will find it necessary to enter into the subject beyond the contents of the present volume.

### XXXVI. *Proceedings of Learned Societies.*

#### ROYAL SOCIETY.

[Continued from p. 237.]

June 11, 1874.—Joseph Dalton Hooker, C.B., President, in the Chair.

THE following communications were read :—

“Spectroscopic Notes.—No. III. On the Molecular Structure of Vapours in connexion with their Densities.” By J. Norman Lockyer, F.R.S.

1. I have recently attempted to bring the spectroscope to bear upon the question whether vapours of elements below the highest temperatures are truly homogeneous, and whether the vapours of different chemical elements, at any one temperature, are all in a similar molecular condition. In the present note, I beg to lay before the Royal Society the preliminary results of my researches.

2. We start with the following facts :—

I. All elements driven into vapour by the induced current give line-spectra.

II. Most elements driven into vapour by the voltaic arc give us the same.

III. Many metalloids when greatly heated, some at ordinary temperatures, give us channelled-space spectra.

IV. Elements in the solid state give us continuous spectra.

3. If we grant that the spectra represent to us the vibrations of different molecular aggregations (this question is discussed in Note II.), spectroscopic observations should furnish us with facts of some importance to the inquiry.

4. To take the lowest ground. If, in the absence of all knowledge on the subject, it could be shown that all vapours at all stages of temperature had spectra absolutely similar in character, then it would be more likely that all vapours were truly homogeneous and

similar among themselves, as regards molecular condition, than if the spectra varied in character, not only from element to element, but from one temperature to another in the vapour of the same element.

5. At the temperature of the sun's reversing layer, the spectra of all the elements known to exist in that layer are apparently similar in character—that is, they are all line-spectra; hence it is more probable that the vapours there are truly homogeneous, and that they all exist in the same molecular condition, than if the spectrum were a mixed one.

6. The fact that the order of vapour-densities in the sun's atmosphere, which we can in a measure determine by spectroscopic observations, does not agree with the order of the modern atomic weights of the elements, but more closely agrees with the older atomic weights, led me to take up the present research. Thus I may mention that my early observations of the welling-up of Mg vapour all round the sun *above the Na vapour* have lately been frequently substantiated by the Italian observers; so that it is beyond all question, I think, that, *at the sun*, the vapour-density of Mg is less than that of Na.

7. The vapour-densities of the following elements have been experimentally determined:—

H	....	1	S	.....	32 (at 1000°)
K	....	39	I	.....	127
As	....	150	Hg	.....	100
Br	....	80	N	.....	14
Cd	....	56	O	.....	16
Cl	....	35.5	P	.....	62

8. To pursue this inquiry the following arrangements have been adopted:—

The first experiments were made last December upon Zn in a glass tube closed at each end with glass plates; and I have to express my obligations to Dr. Russell for allowing them to be conducted in his laboratory, and for much assistance and counsel concerning them.

A stream of dry H was allowed to pass. The tube was heated in a Hofmann's gas-furnace, pieces of the metal to be studied having previously been introduced. It was found that the glass tube melted; it was therefore replaced by an iron one. The inconvenience of this plan, however (owing to the necessity for introducing the metal into the end of the hot tube when the first charge had volatilized), and, moreover, the insufficiency of the heat obtainable from the gas-furnace, soon obliged me to replace both tube and furnace by others, which have now been in use for many weeks, and which still continue to work most satisfactorily.

The iron tube is 4 feet in length, and is provided with a central enlargement, suggested to me by Mr. Dewar, forming a T-piece by the screwing in of a side tube, the end of which is left projecting from the door in the roof of the furnace. Caps are

screwed on at each end of the main tube ; these caps are closed by a glass plate at one end, and have each a small side tube for the purpose of passing hydrogen or other gases through the hot tube. The furnace is supplied with coke or charcoal ; an electric lamp, connected with thirty Grove's cells, is placed at one end of the tube and a one-prism spectroscope at the other. The temperatures reached by this furnace may be conveniently divided into four stages :—

I. When the continuous spectrum of the tube extends to the sodium-line D, this line not being visible.

II. When the continuous spectrum extends a little beyond D, this line being visible as a bright line.

III. When the spectrum extends into the green, D being very bright.

IV. When the spectrum extends beyond the green and D becomes invisible as a line, and the sides of the furnace are at a red heat.

I may add (1) that I have only within the last few days been able to employ the third and fourth stages of heat, as the furnace was previously without a chimney, and the necessary draught could not be obtained ; and (2) that I was informed, a little time ago, by Prof. Roscoe that, with a white-hot tube, he had observed new spectra in the case of Na and K. These spectra, which I now constantly see when these temperatures are reached, I shall call the "new spectra."

9. The results of the experiments, so far as the visible spectrum is concerned, between the stages indicated may be stated as follows :—

H. No absorption.

N. No absorption.

K. I have observed, either separately or together :—

( $\alpha$ ) The line absorption-line near D.

( $\beta$ ) Continuous absorption throughout the whole spectrum.

( $\gamma$ ) Continuous absorption in red and blue at the same time, the light being transmitted in the centre of the spectrum (as by gold-leaf).

( $\delta$ ) Continuous absorption clinging on one side or other of the line. (This phenomenon, which, so far as I know, is quite new, will be described in another note.)

( $\epsilon$ ) The new spectrum.

Na. I have observed, either separately or together :—

( $\alpha$ ) D absorbed.

( $\beta$ ) Continuous absorption throughout the whole spectrum.

( $\gamma$ ) Continuous absorption clinging on one side or the other of D.

( $\delta$ ) The new spectrum.

Zn. Continuous absorption in the blue. (An unknown line sometimes appears in the green, but certainly no line of Zn.)

Cd. Continuous absorption in the blue.

Sb. New spectrum, with channelled spaces and absorption in the blue.

P. The same. (This, however, in consequence of the extreme delicacy of the spectrum, requires confirmation.)

S. Channelled-space spectrum (previously observed by Salet).

As. Probable channelled-space spectrum. (Observations to be repeated.)

Bi. No absorption.

I. Channelled spectrum in the green and intense bank of general absorption in the violet, where at the ordinary temperature the vapour transmits light.

Hg. No absorption.

10. These results may be tabulated as follows :—

	V. d.	Modern atomic weight.	
H ....	1	1	No visible absorption.
K ....	39	39	Line absorption.
As ....	150	75	Probable channelled-space absorption.
Cd ....	56	112	Continuous absorption in the blue.
I ....	127	127	Channelled-space absorption + band of absorption in violet.
Hg ....	100	200	No absorption.
N ....	14	14	" "
P ....	62	31	Channelled-space spectrum probable.
Na ....	(?)	23	Line absorption.
Zn ....	(?)	65	Continuous absorption in the violet.
Sb ....	(?)	122	Channelled-space spectrum and absorption in the blue.
S ....	32	32	Channelled-space spectrum.
Bi ....	(?)	208	No absorption.

11. It will be seen from the foregoing statement that if similar spectra be taken as indicating similar molecular conditions, then the vapours, the densities of which have been determined, have not been in the same molecular condition among themselves. Thus the vapours of K, S, and Cd, at the fourth stage of heat, gave us line, channelled-space, and continuous absorption in the blue respectively. This is also evidence that each vapour is non-homogeneous for a considerable interval of time, the interval being increased as the temperature is reduced.

"Spectroscopic Notes.—No. IV. On a new Class of Absorption Phenomena." By J. Norman Lockyer, F.R.S.

1. In the experiments on the absorption-spectrum of Na and K vapour heated in a red-hot tube, to which further reference is made in separate notes, I have observed phenomena quite new

to me, some rough drawings of which I lay herewith before the Royal Society. As the phenomena are only momentary, I cannot answer for the final accuracy of the drawings, nor have I been able to represent the softness of the gradations of shade.

2. In the drawings, the red end of the spectrum is to the left; the D line common to them all is the image of a slit about half an inch long, on which slit the light falls from an electric lamp, through the tube and chamber in which the vapours are produced. The lower part of the drawings would generally represent, therefore, the spectrum of the *less dense vapours* were the vapours at rest.

3. One of the phenomena referred to consists of what may be described as a unilateral widening of the line D: the side absorption, however, is much less dense than that of the line; it is bounded by D on one side and by a curved line on the other. Figs. 1, 2, and 3 will give an idea of this appearance in three stages as it is frequently actually seen, *i. e.* as the absorption travels up or down the line it widens as shown.

Fig. 1.

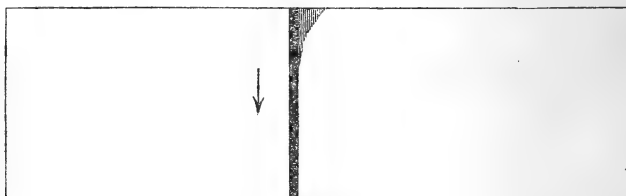


Fig. 2.

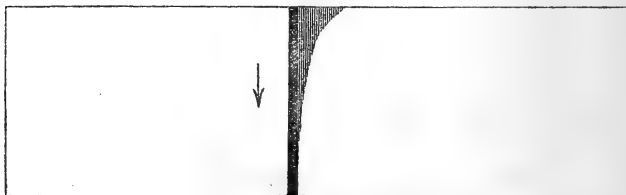
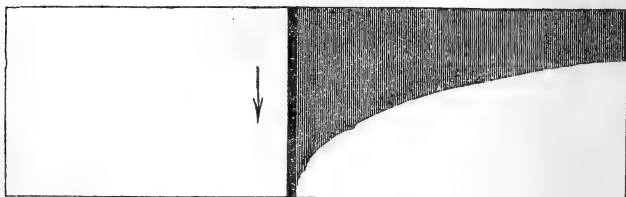


Fig. 3.



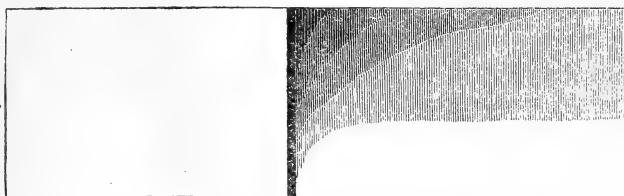
4. Figs. 4 and 5 give two variations sometimes observed—fig. 4 showing the darkening in the absorption and an increased steepness in the curve; fig. 5 the simultaneous existence of apparently different absorptions, all bounded by D on one side, but by different curves on the other, and being of different intensities.



Fig. 4.



Fig. 5.



5. Although, in the preceding drawings, I have represented this unilateral widening exclusively on the more refrangible side of D, I have observed it on the other, though scarcely so frequently.

6. Accompanying these appearances, but generally best visible when the absorption with curved boundary is visible on both sides of D, is a brilliant boundary replacing the mere change of shade.

7. At times the brilliant boundary is continuous across D, as shown in fig. 6; but I append figs. 7 and 8 to show that the phenomena on either side of D are independent of each other.

Fig. 6.

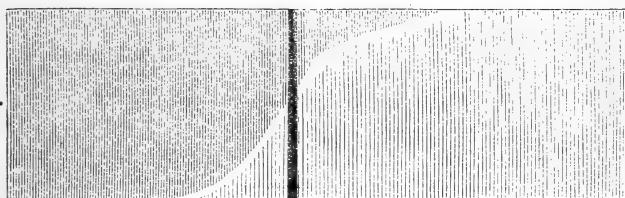


Fig. 7.

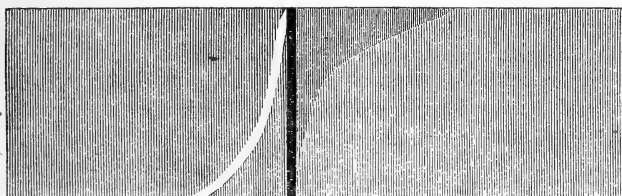
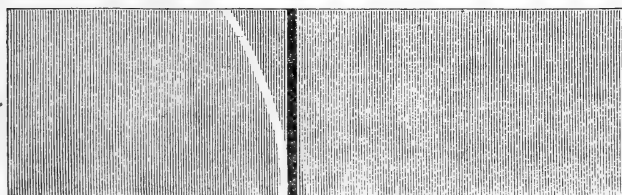


Fig. 8.



8. At times, D puts on the appearance of the limiting line of a channelled-space spectrum, the "easing off" of the absorption being now on one side and now on the other.

9. Should all these phenomena be ultimately referred to the causes which produce a channelled-space spectrum (one of which undoubtedly is the tendency to a unilateral instead of a bilateral widening), a line-spectrum will be regarded as a special case merely, and not as an entirely different spectrum, as it has been hitherto; and the range of molecular combinations in any one element from which line-spectra may be produced is extended.

10. The question further arises, whether many of the short lines in spectra are not remnants of channelled-space spectra.

June 18.—Joseph Dalton Hooker, C.B., President, in the Chair.

The following communication was read :—

"Researches in Spectrum-Analysis in connexion with the Spectrum of the Sun."—No. IV. By J. Norman Lockyer, F.R.S.

Maps of the spectra of calcium, barium, and strontium have been constructed from photographs taken by the method described in a former communication (the third of this series). The maps comprise the portion of the spectrum extending from wave-length 3900 to wave-length 4500, and are laid before the Society as a specimen of the results obtainable by the photographic method, in the hope of securing the cooperation of other observers. The method of mapping is described in detail, and tables of wave-lengths accompany the maps. The wave-lengths assigned to the new lines must be considered only as approximations to the truth. Many of the coincidences between lines in distinct spectra recorded by former observers have been shown, by the photographic method, to be caused by the presence of one substance as an impurity in the other; but a certain number of coincidences still remain undetermined. The question of the reversal of the new lines in the solar spectrum is reserved till better photographs can be obtained.

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#### GEOLOGICAL SOCIETY.

[Continued from p. 243.]

May 27th, 1874.—John Evans, Esq., F.R.S., President,  
In the Chair.

The following communications were read :—

1. "On the last Stage of the Glacial Period in North Britain."  
By T. F. Jamieson, Esq., F.G.S.

In this paper the author arranged the Glacial phenomena of Scotland under the following three heads :—

1. The great early glaciation by land-ice (maximum effects of glaciation).
2. The period of glacial marine beds containing remains of Arctic Mollusca, when most of the country was covered by the sea.

3. The time of the late glaciers, the special subject of the paper.

After expressing himself in opposition to the hypothesis of a great polar ice-cap, the author described this last period as one not of mere local glaciers, but as characterized by a return of a great ice-sheet over nearly the whole of Scotland and Ireland; but he stated that this ice-sheet was probably neither so thick, so extensive, nor so enduring as that of the first period of glaciation, which cleared away every thing in the shape of superficial deposits down to the hard rock. He believed, however, that in the last period the mountains of Scotland and Wales, as well as the Pennine range and the rest of the north of England as far as Derby, were covered with thick ice, which in most parts reached down to the sea, and that extensive snow-beds prevailed over the rest of England. In the summer months the melting of these would give rise to streams of muddy water, and produce the superficial deposits of Brick-earth, Warp, and Loess; whilst, when the currents were stronger, perhaps from the thaw being unusually rapid, deposits of gravel would be formed. This second ice-sheet would gradually become less and break up into valley-glaciers, which in their retreat would leave kaims and eskers at low levels, and moraines in the mountain-glens. During this time no new great submergence of the country took place; and the last great modifications of the surface were sub-aërial, and not submarine, the work having been done by frost, rain, and glaciers.

2. "Notes on the Upper Engadine and the Italian Valleys of Monte Rosa, and their relation to the Glacier-erosion Theory of Lake-basins." By the Rev. T. G. Bonney, M.A., F.G.S.

The author stated that he had examined:—(1) the small lakes on the summit of the Bernina Pass. These were situated in a position very favourable to glacier-erosion, and, he thought, might be attributed to that cause. (2) The lakes on the upper part of the Maloya Pass. These lay in three rock-basins, and at first sight seemed favourable to the glacier-erosion theory; but further examination showed that they were in no way connected with the glacial system of the neighbourhood, and were probably preglacial. (3) The Val Bregaglia to the Lake of Como. The presence of barriers in the valley, its frequent V-like form, and the signs of glacial action to near the present level of the stream, seemed to indicate that the glacier had had but slight erosive power. (4) The Como arm of the lake. It was shown that the glacier which was supposed to have excavated the lake had passed over the ridge of Nagelfluhe and Molasse that encloses it, and had not been able to grind away its remarkably sharp crest. (5) Similar evidence was produced with regard to the Lake of Orta. (6) The Italian valleys E. of Monte Rosa. These were shown to offer difficulties precisely similar to those of the Val Bregaglia. The author therefore argued that these cases showed how superficial the action of the glaciers had been, and that they must have been wholly inadequate to excavate the greater lake-basins,

since no approach to this form, no U-like trough, was found in the valleys down which the glaciers had flowed on their way to the lakes. As, then, the principal features of the district appeared to be preglacial, he contended that disturbances of the beds of the valleys along lines transverse to their direction were more likely to have produced the lakes.

June 10th, 1874.—John Evans, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "On the occurrence of Thanet beds and of Crag at Sudbury, Suffolk." By William Whitaker, Esq., B.A., F.G.S.

After referring to some passages in papers by Mr. Prestwich, in which the probable existence of Thanet beds in North Essex is mentioned, the author described certain sections near Balingdon, on the right bank of the Stour, which exhibit sands belonging to this series. The principal section at the Great Chalk-pit, Balingdon, shows, in descending order, beds belonging to the London Clay, Reading beds 9 feet, and Thanet sands about 14 feet, resting on Chalk. No fossils occur in the Thanet beds; and their identification is founded on the uniformity in the character of the sands, their resemblance in fineness, compactness, and colour to the Thanet sands of West Kent, the presence at the base of the series of a green-sand resembling the "base-bed" of the Thanet sand, and the occurrence immediately beneath it of a layer of tabular flint, as is usual where the Thanet sand caps the chalk.

The Crag-beds described by the author are found on the left bank of the Stour, in Suffolk, and consist of ferruginous dark reddish-brown sand, with layers of ironstone, slightly false-bedded, with here and there light-coloured grit with broken shells. In the lower part there are layers of flint pebbles, phosphatic nodules, and phosphatized bones, which also form a bed about 1 foot thick at the bottom. These beds rest on deposits belonging to the lower portion of the Thanet sands, and these again on the Chalk. In one pit a considerable number of fossils occur, but not in a condition to enable them to be satisfactorily determined. From their position and general characters these beds were referred by the author to the Red Crag.

2. "Note on a modified form of Dinosaurian ilium, hitherto reputed Scapula, indicative of a new genus, or possibly of a new order of Reptiles." By J. W. Hulke, Esq., F.R.S., F.G.S.

The author reexamines Mantel's "Scapula of an unknown Reptile"—Owen's "Scapula of *Megalosaurus*?", and adduces reasons for considering it to be a modified Dinosaurian ilium. He describes two new examples of the bone in Dr. Wilkins's collection, contrasts them with undoubted scapulæ of sundry Dinosaurs and existing reptiles, and proves their essential correspondence with the ilia of known Dinosaurs.

3. "Note on a Reptilian Tibia and Humerus (probably of *Hylæosaurus*), from the Wealden Formation in the Isle of Wight." By J. W. Hulke, Esq., F.R.S., F.G.S.

In this communication the author describes two saurian limb-bones, remarkable for the great expansion of their articular ends, and the shortness and smallness of their shaft. The features of the tibia are more like those of the tibia of *Hylæosaurus* than of any other Dinosaur. This resemblance, and the suitability of the humerus to the very massive articular end of the Hylæosaurian scapula, dispose the author to refer the bones to this Saurian.

### XXXVII. Intelligence and Miscellaneous Articles.

#### ON THE MAGNETIZING-FUNCTION OF TEMPERED STEEL.

BY E. BOUTY.

THE magnetic moment of a magnetized needle may always be regarded as the product of two factors, of which the one expresses the quantity of magnetism contained in the needle (or, if preferred, the power of each pole), while the other factor is equal to the distance of the poles. By the advice of M. Jamin I applied myself to determine these two distinct elements separately, and to study apart the variation of each of them when the conditions of magnetization are changed. The following is the principle of the method employed.

It is easy to verify that the magnetic moments  $y$  of a series of needles of different lengths  $x$ , magnetized under the same conditions, can be represented by a formula such as

$$y = m(x - d), \quad \dots \dots \dots (1)$$

provided that their lengths exceed a certain limit  $l$ . In all these needles the quantity of magnetism is constant and equal to  $m$ , and the distance of the poles from the extremities is also constant and equal to  $\frac{d}{2}$ . If we break these needles and take from their middle

parts various fragments of lengths exceeding another limit  $l' < l$ , their moments  $y'$  are represented by the formula

$$y' = m(x' - \delta): \quad \dots \dots \dots (2)$$

the quantity of magnetism is the same as in the mother needle; but the poles are nearer to the extremities,  $\delta$  being always less than  $d$ . These facts, almost evident *à priori*, have been carefully verified by experiment.

Suppose now that  $m$  and  $d$  are to be determined for a given needle. We first ascertain its magnetic moment  $y$ ; it is then reduced by the removal of a sufficient length from both ends, and the new magnetic moment  $y'$  determined. We know \* that in rupture-needles of the same diameter the quantity  $\delta$  is constant, whatever the intensity of the magnetization; its value, known beforehand, is, for instance, 5.5 millims. in needles of 0.553 millim. diameter.

\* "Studies on Magnetism," III., Phil. Mag. March 1875, pp. 188-191. Phil. Mag. S. 4. Vol. 49. No. 325. April 1875. Z

Besides, we can shorten the primitive fragment by successive breakings, and thus fix as many points as we will of the right line represented by equation (2): the quantity of magnetism will be obtained with great exactness.

The determination of  $d$  is much less precise, since for settling its value we have only one observation, that which refers to the mother needle, and moreover  $d$  is always very small. Still, by multiplying observations and taking their means we arrive at satisfactory results.

By means of this method I have studied the manner in which the quantity of magnetism and the distance of the poles vary when needles 0.553 millim. in diameter, tempered very hard, are magnetized by being passed through one and the same spiral, and the intensity of the current is varied.

*Quantities of magnetism.*—The average results obtained are represented in the following Table, the numbers in both columns being expressed in arbitrary units.

Intensity of the current.	Quantity of magnetism.
3 .....	hardly perceptible.
5 .....	0.12
7 .....	0.51
9 .....	1.09
12 .....	2.11
13.8 .....	2.89
15 .....	3.35
18 .....	5.65
23 .....	11.96
28 .....	17.90
36 .....	23.00
40 .....	24.00
50 .....	25.90
$\infty$ .....	28.90

Several physicists, amongst others Stoletow\* and Rowland†, have recently applied themselves to the determination of what the former calls the “magnetizing-function” of various sorts of iron or steel; it is the ratio  $\frac{H}{F}$ , of the quantity of magnetism  $H$  developed

either temporarily or permanently in unit volume of the substance taken under the form of a cylinder of infinitesimal transverse dimensions in proportion to its length, to the force  $F$  which produces the magnetism by acting in the direction of the axis of the cylinder. The clearest way of representing this function consists in constructing a curve the ordinates of which are the quantities  $H$ , and its abscissæ the forces  $F$ . At first concave towards the positive ordinates, it afterwards presents a point of inflection and approaches asymptotically towards a parallel to the axis of the abscissæ.

The numbers contained in the preceding Table are proportional

\* Philosophical Magazine, January 1873.

† Ibid, August 1873.

to F and H. The curve given by them presents the same general characters as do Stoletow and Rowland's curves, but with more rigid turns, a concavity towards the positive H strongly pronounced for small values of F, an inflection so elongated that for a considerable portion of its extent the curve is indistinguishable from a straight line; in a word, it has the appearance of a broken line with the obtuse angles much rounded: such are the results given by the construction of the new curve. They confirm the facts discovered by entirely different methods in the case of iron, at the same time that they characterize the peculiar consistence of very stiffly tempered steel, and supply an unexpected verification of the theoretic ideas I have put forth elsewhere on the subject\*.

Finding it impossible to effect absolute measurements, I could do no more than compare Rowland's results with mine, in the manner indicated by the following Table. C is the abscissa at the origin of the tangent to the point of inflection, C' the abscissa of the point where the tangent meets the asymptote to the curve, L the maximum of magnetization. All the ordinates are expressed as functions of C, all the abscissæ as functions of L.

	Iron, according to Rowland.		Chilled steel.	
	Abscissæ.	Ordinates.	Abscissæ.	Ordinates.
Abcissa C' and corresponding ordinate of the curve .....	1·973 C <sub>1</sub>	0·633 L <sub>1</sub>	2·608 C <sub>2</sub>	0·796 L <sub>2</sub>
Ordinate corresponding to the abscissa C .....	.....	0·100 L <sub>1</sub>	.....	0·100 L <sub>2</sub>
Coordinates of the point of inflection .....	1·271 C <sub>1</sub>	0·278 L <sub>1</sub>	1·667 C <sub>2</sub>	0·414 L <sub>2</sub>
Length of the rectilinear portion of the curve (difference of the extreme abscissæ) .....	0·190 C <sub>1</sub>	.....	0·509 C <sub>2</sub>	.....

The interval from C to C' might be named *interval of rapid magnetization*. Within these limits, distant 0·973 C<sub>1</sub> for iron, 1·608 C<sub>2</sub> for chilled steel, the quantity of magnetism increases from  $\frac{1}{10}$  of its maximum value up to nearly  $\frac{2}{3}$  for iron and  $\frac{4}{5}$  for steel. The determination, in absolute value, of C, C', and the corresponding ordinates would furnish a good comparison of the magnetic powers of different kinds of steel, iron, &c., and at the same time would fix the limits which it would be absurd not to reach, or not economical to exceed, in the intensity of the currents employed for the magnetizing.

In a future communication I shall indicate the results regarding the distance of the poles, as well as the changes produced in the quantity of magnetism or in the polar distance when the needle is passed repeatedly through the magnetizing spiral.—*Comptes Rendus de l'Académie des Sciences*, vol. lxxx. pp. 650–653.

\* "Studies on Magnetism," IV., Phil. Mag. March 1875, p. 199 et seqq.

ON THE DEPENDENCE OF THE COEFFICIENT OF FRICTION OF ATMOSPHERIC AIR ON TEMPERATURE. BY ALBERT VON OBER-MAYER, CAPTAIN OF ARTILLERY.

Of the two hypotheses from which the dynamical theory of gases starts, the older gives the coefficient of friction of gases proportional to the square root, the newer (Maxwell's) gives it proportional to the first power of the absolute temperature. From the retardations of vibrating disks by the friction of the air, Maxwell found experimentally the power 1, O. E. Mayer the power  $\frac{3}{4}$ ; by experiments on currents through capillary tubes O. E. Mayer found the power  $\frac{3}{4}$ , J. Puluj the power  $\frac{2}{3}$ , of the absolute temperature.

For the more certain determination of the ratio, experiments on currents through four capillaries of glass and one of brass were undertaken; and together with the temperature of the room those of boiling water, congealing paraffin, and a mixture of salt and snow were employed. A first series of experiments, less accurate, were carried out with the difference of pressure variable; a second, considerably more exact, with the difference constant.

The results of the two series agree very well, and confirm those of Mayer's experiments in a perfectly satisfactory manner. For the coefficient of friction  $\mu$  at the temperature  $t$  there were found:—

According to the first series,  $\mu = 0.0001706 (1 + 0.002735 t)$ ;

„ „ second „  $\mu = 0.00016747 (1 + 0.002723 t)$ .

—*Kaiserliche Akademie der Wissenschaften in Wien, Sitzung d. math.-naturw. Classe, Feb. 4, 1875.*

ON CAMACHO'S NEW ELECTROMAGNET.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

General Post Office,  
March 2, 1875.

Camacho's concentric-tube electromagnet seems to be identical in principle with one lent me when I lived in Manchester about 1852, by the late Richard Roberts, so well known in connexion with spinning-machinery.

His electromagnet was an iron cube sawn nearly through by a number of parallel cuts, crossed at right angles by other cuts, so as to form a series of cores connected at one end.

Each of the cores was wrapped with wire, forming a series of electromagnets, connected by a common breech piece in metallic connexion with all the cores.

This arrangement was very powerful for its size; I regret that I have no note of its performance.

Yours faithfully,  
R. S. CULLEY.



THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FOURTH SERIES.]

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MAY 1875.

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XXXVIII. *On Spectra of Gases.* By M. EUGEN GOLDSTEIN\*.

WÜLLNER has recently published some experiments from which he concludes that the appearance of different spectra of one and the same gas does not depend on the temperature.

It is known that the complete spectra of the gases have hitherto only been produced by means of electrical discharges; and we are accustomed to distinguish two different kinds of discharges, the continuous discharge and the disruptive discharge.

Discharges which we call continuous show in a mirror rotating about thirty times a second the image of a continuous field of light. I will not decide whether this discharge is really continuous, or whether it consists of sparks following each other so rapidly that the rotating mirror cannot resolve them into separate images, at least not with the velocities which we can conveniently give to the mirror. This latter opinion, which Professor Helmholtz considers to be the more probable one, is suggested by the fact that just those means by which we can shorten the time elapsing between the different discharges, lead at the end to the so-called continuous discharge. The temperature is doubtless the greater the more electricity passes in a single discharge. It is therefore higher in discharges following each other slowly than in the continuous discharge. The measurements made by Riess with the electrical thermometer agree with this.

According to Wüllner, the two forms of spectra which are called by Plücker and Hittorf spectra of the first and second

\* Communicated by Dr. Arthur Schuster, from Poggendorff's *Annalen*, vol. cliv. pp. 128-149.

order, or band- and line-spectra, are closely related to the modes of discharge. He believes he has established by a series of experiments "that the line-spectrum of a gas only appears in the disruptive discharge, the band-spectrum only in the continuous discharge through the gas." After these facts have been established, Wüllner tries to explain the spectra of different orders by means of the different thicknesses of the luminous layer in the two modes of discharge. In the disruptive discharge (according to Wüllner) only a few molecules of the gas emit light; in the continuous discharge, on the other hand, nearly the whole mass of the gas contained in the spectral tube is luminous. If we accept the principles deduced by Zöllner, the gas-spectrum can only consist of a few luminous lines in the first case, while the thick layer of the continuous discharge will show light of all wave-lengths which the gas can emit at the temperature in question. I shall now give the results of observations and experiments which were made in reference to the above assertions.

The close relation between the two modes of discharge and the two kinds of spectra which seemed to be established by Wüllner's experiments, became first doubtful to me in working with a tube filled with air under low pressure and with a Leyden jar inserted between one of its electrodes and the induction-coil. The image of the discharge in a rotating mirror showed, besides continuous fields, groups of images of the tube *not wider* than the tube itself.

The observations were at first made with a mirror rotating about four times a second, but were repeated with a velocity about twenty-five times as great. The spectroscope showed only the *band-spectrum* of nitrogen. Geissler's tube filled with *hydrogen*, on the other hand, the capillary portion of which showed the characteristic red colour when the spark was passing, gave only widened fields in the rotating mirror, the colour of which was everywhere of the same crimson colour. The spectrum consisted of the well-known *lines* of hydrogen. A number of other tubes filled with hydrogen gave the same result. Both experiments contradict directly the law given by Wüllner. In order to arrive at a definite conclusion, a close investigation seemed to be necessary.

During the course of my experiments I found it often necessary to introduce into the circuit a layer of air, which was sometimes replaced by a second tube filled with air under high pressures. In these cases the tube filled with air under low pressure always shows the band-spectrum; the spark in air, as well as in the second spectral tube, shows the line-spectrum.

If we take the views of Wüllner as proved, we must assume

that the discharge can be disruptive in one part of the circuit and continuous in the other part. We must therefore investigate the question whether the discharges go through adjacent parts of the same circuit in the same rhythm or not, in order to be able to decide whether Wüllner's hypothesis can be correct.

If we take an analogy in the flow of an incompressible liquid, the isochronism of the discharge in different parts of the same circuit is self-evident. The experimental investigation gave the following results.

The rotating mirror showed that if the exhausted tube was at the same distance as the spark, both images were of the same width. If the discharge through air under atmospheric pressure begins, as shown by Lissajous, by a spark followed by the aureola, the image of the spectral tube begins with a luminous band, the width of which remains constant, whatever the velocity of the mirror may be.

When the discharge in the air consisted of several partial discharges, the same number of narrow images of the tube were seen at corresponding distances.

The image of the discharge through a vacuum-tube is, when the remaining circuit is metallic, very complicated, consisting of fields of different brightness, &c. Two or more tubes put into the same circuit, even if the gas in the different tubes is chemically different (*e. g.* nitrogen and carbonic acid), always give exactly the same image, showing in every detail the same groups of illuminated fields and the same variation in brightness. The exact coincidence of rhythm and intensity in the same discharge, according to these experiments, is evident.

A tube filled with carbonic oxide which is in my possession allows only sparks to pass; every discharge of the induction-coil is subdivided into a greater or smaller number of sparks. This tube was inserted in the circuit together with other tubes containing nitrogen. These nitrogen-tubes separately allowed a continuous discharge to pass; but when the carbonic-oxide tube was introduced, sparks only passed, the same number as in the carbonic-oxide tube.

A Leyden jar gives very strong sparks; the effect of the induction-spark (which allows only a small quantity of electricity to pass) will only show quantitative differences compared with the discharge from a battery of Leyden jars, and will be about the same as the discharge from a small jar.

If the electricity goes through the whole circuit in the same rhythm, the introduction of a small spark through air will have the same effect as a condenser which is feebly charged.

The introduction of a condenser changes the reddish colour of the positive light seen in narrow tubes into blue. The introduction of a spark will give the same result.

The discharge of a Leyden jar does not generally show any stratifications, even if the positive light without the jar shows them. If we introduce into a circuit containing a tube showing stratified light a spark in atmospheric air, and look at the image of the discharge in a rotating mirror, we shall see that the image begins with a band which we cannot widen by increasing the number of rotations of the mirror; and this band is *not* stratified. If we do away with the spark, the image of this band will again be stratified.

If a Leyden jar is introduced into the circuit, the resistance of which is somewhat large, the dark space which is generally seen between the positive and negative light disappears, and the whole tube is filled with light of the colour of the positive light. Introducing a spark instead of the jar, we observe light in the dark space, the intensity of which varies with the strength of the spark.

The images given by the rotating mirror are characteristic in this case. The blue light in the negative cylinder of a spectral tube of the common form is widened into a field of light, the intensity of which becomes so small, if the velocity of rotation is sufficiently great, that the eye cannot distinguish it; the dark space extends from the negative light to the capillary part of the tube. On the other hand, feeble light fills the positive tube, which can be made to sink below the limit of visibility in the rotating mirror. We thus get a good image of the discharge from the capillary part only, showing a long band, the width of which is equal to its length. The image just described corresponds to the continuous discharge. When a spark is introduced into the circuit, both cylinders are illuminated, and we see the complete image of the whole tube flashing in. The difference between a continuous and discontinuous discharge is here seen in a striking way. Spark and jar produce here again the same effect.

The discharge of a Leyden jar in thick sparks is affected in a curious way by the magnet. The discharge shows every where the colour of the positive light, and is torn into two parts which run along opposite sides of the tube. Each part, however, has a different character according as it emanates from the positive or negative end of the tube. An explanation of this fact by means of oscillating discharges does not seem possible.

The positive light of a continuous discharge, on the other hand, is deflected as a continuous thread towards one side. If we introduce a spark in air sufficiently long, the discharge is torn again into two parts, and the whole phenomenon is the same as if a Leyden jar were introduced.

I think I may consider it to have been proved by these and

similar observations that the discharge is at the same time every where the same throughout the whole circuit, and that therefore it cannot be continuous in one part and discontinuous in another.

I now turn to the spectra we observe in these different kinds of discharges.

I must first mention an observation regarding a change in the discharge without the aid of any of the means mentioned above.

The tube filled with carbonic oxide, which has already been mentioned, showed in the beginning stratifications with a dark space and feeble light. The discharge was widened into a continuous band in the rotating mirror.

The spectrum of carbonic oxide consists of a well-known group of bands. After a short time the phenomena characteristic of the continuous discharge disappeared, and the rotating mirror showed distinct images of the tube indicating a disruptive discharge. Nevertheless the spectrum consisted of the previously mentioned bands without the addition of lines.

Tubes filled with nitrogen show generally the band-spectrum. When the discharge was made disruptive by means of the carbonic-oxide tube, the spectrum of nitrogen remained the same, only showing a variation of intensity.

A tube filled with nitrogen and another filled with hydrogen were introduced into the same circuit. The spectrum of nitrogen consisted of bands; the spectrum of hydrogen showed  $H\alpha$ ,  $H\beta$ ,  $H\gamma$ . If Wüllner's hypothesis were correct, such a result would be impossible; both tubes, according to Wüllner, should give spectra of the same order. The images of both tubes in the rotating mirror consisted of a continuous field of light.

If one of the electrodes of a vacuum-tube has only a small surface, or if it is contained in a narrow tube, the spectrum may be different, according to the direction of the current. If the large electrode is positive, the discharge consists of a greater or smaller number of single sparks; if the current goes in the other direction, the discharge is continuous.

If we introduce such a tube into the circuit together with another tube, the discharge, as has been said, is continuous or disruptive according to the direction of the current, yet the spectrum of the other tube is unaltered. It often happens that in one and the same tube both spectra are seen at the same time, the narrow part of the tube showing the line-spectrum, while the wider parts of the tube show the band-spectrum; yet the discharge has every where the same character.

If the gas in a tube is exhausted to very small fractions of a millimetre pressure, the discharge consists of a number of sparks

which the mirror cannot widen. The spectrum, however, remains the same. If under higher pressure it was a band-spectrum, it will remain so.

If the intensity of the current decreases, the continuous discharge often alternates with sparks—as, for instance, if the closing of the inducing current happens to be bad or too short. Artificial strengthening of the current does away with these sparks; the introduction of moist resistances increases their number. The spectra do not change if this takes place. Very often these sparks pass at the beginning of the discharge, or after having changed the direction of the current. The band-spectrum of air, of carbonic oxide, &c. in all these cases is permanent.

(As the introduction of a spark in the external air generates in the rotating mirror another image of the discharge, which to the eye is superposed on the continuous discharge, it is not advisable to do away with the closing-current by means of a spark in the air. This is best done by means of tubes which only allow the opening-current to pass.)

If the vacuum-tube contains moist air, the spectrum shows the lines of hydrogen together with the bands of air. According to Wüllner's theory, only the continuous discharge can produce the band-spectrum of air, while only the disruptive discharge can produce the line-spectrum of hydrogen. The rotating mirror should therefore show sharply defined images of the tube due to the disruptive discharge of hydrogen, and at the same time broad fields due to the continuous discharge through air. This, however, is not the case; the mirror only shows uniform fields, proving that there is only a continuous discharge passing, and that therefore the hydrogen lines can be produced by a continuous discharge.

A tube filled with hydrogen under low pressure mixed with a convenient quantity of oxygen gives out a magnificent crimson light when the induction-current passes. No bands are seen; neither, as a rule, are any lines visible which are not due to hydrogen. (In some cases two greenish yellow lines could not be eliminated.) The rotating mirror shows that the discharge is continuous.

If we slacken the speed of the interruptor of a Ruhmkorff's coil, the intensity of the light given out by a vacuum-tube increases up to a certain point. Looked at through the spectroscope, the hydrogen-lines are seen to flash in with great intensity with every opening-current. The rotating mirror shows that at the same time the *long continuous band* increases in intensity. The discharge, therefore, is still continuous. It can be directly shown that band- and line-spectra may be

given out by the same discharge. If we cover a vacuum-tube with lampblack and make only a small scratch in the lampblack through which the light can pass, this point is drawn out into a line by means of the rotating mirror. This line can be looked at by means of a small prism, the edges of which are placed parallel to its length. We then see, for instance, if the tube is filled with hydrogen, bands and lines throughout the extent of the line of light. If the tube is filled with moist air, the bands of nitrogen are seen everywhere together with the lines of hydrogen.

Experiments with the Leyden jar also show that Wüllner's hypothesis does not agree with facts.

The discharge of a Leyden jar consists, like that of an induction-coil, of a spark, and of an aureola which can be blown away by means of a current of air, or separated from the spark by means of a rotating mirror. If a Leyden jar is discharged through a tube filled with rarefied nitrogen, only the band-spectrum is seen if the pressure is conveniently chosen. The rotating mirror shows, however, that the discharge is composed of a continuous part and a disruptive spark.

If we increase the resistance, the continuous part of the discharge is weakened and finally becomes invisible; yet only the band-spectrum is seen. It may be said that the continuous discharge is so much weakened by the broadening effect of the rotating mirror that it cannot be seen any more in the mirror, yet it might be strong enough in the tube itself to give a band-spectrum. This objection is easily answered. We can find an arrangement which allows us to look at the image of the spark in the rotating mirror through a prism, and we shall see that it is just that spark which gives the band-spectrum.

If the resistance is pretty great, the line-spectrum begins to appear together with the band-spectrum. It is still possible by regulating the resistance to reduce the discharge as seen in the rotating mirror to a single image; and this image shows, when looked at by means of the spectroscope, the lines and bands of air at the same time.

The same results are arrived at with hydrogen. The discharges through the vapours of sodium and mercury are widened by means of the rotating mirror, and allow, therefore, a continuous discharge to pass. It is well known that these substances give a line-spectrum.

If we introduce into the circuit of a Ruhmkorff's coil two tubes both filled with air, but of different diameters, we can, by conveniently regulating the pressure, produce the band-spectrum in one of the tubes and the line-spectrum in the other. It is easily proved by means of the rotating mirror that the discharge has exactly the same character in both tubes.

A tube which has different widths in different parts shows sometimes, when the discharge is disruptive, the line-spectrum at the poles (which are generally introduced into the wider part of the tube); the remaining part of the wider end gives the band-spectrum; and the narrow part shows again the line-spectrum. The rotating mirror shows, as was to be expected, that the discharge is the same in all parts of the tube.

The discharge of a Leyden jar in air under rather high pressure shows sometimes a strange phenomenon. Near to the negative end of the tube appears a place which is of yellowish pink colour. The spectrum-analysis of this point gives the bands of nitrogen; the remaining part of the tube shows only the lines of nitrogen. The rotating mirror gives the image of the tube together with its pink point as one whole. (Velocity of rotation about 40 per second.)

The spectrum of the pink point makes rather the impression of a continuous spectrum. The bands are wide and indistinct; if the phenomenon is at its best, only the blue and violet bands can be distinguished from the illuminated ground. I shall try further on to give an explanation of this phenomenon.

I believe it to be established by the above experiments, that the different spectra have nothing to do with the mode of discharge.

I could not confirm by experiment the second proposition of Wüllner—"In the disruptive discharge only a few molecules, therefore a very thin stratum of the gas, is luminous." I could obtain sparks in rarefied gas as much as several centimetres in diameter. The colour of such sparks in air is blue or pink, with the various tints which can be produced by changes in intensity and saturation of these colours.

The colours of thick sparks in hydrogen are bluish white, flesh-coloured, yellowish, yellowish red, and crimson.

Not only are those sparks thick which give the band-spectrum, but also those (and it is of these Wüllner was thinking) which give a line-spectrum.

By introducing sparks and jars in the outer circuit, we may succeed in obtaining sparks blue in air and red in hydrogen which give line-spectra, and which filled entirely tubes of  $1\frac{1}{2}$  centim. diameter. I shall mention subsequently observations on the negative light which refer to this point.

Another assertion of Wüllner's says that the band-spectrum is always produced by a thick discharge. Part of the above can already be produced as evidence to the contrary. In capillary tubes band-spectra are seen, while line-spectra may be given out by much thicker layers of air.

The induction-spark in air under ordinary pressure, which is



white and surrounded by an aureola, does not appear suddenly if the pressure of the gas under low pressure is increased slowly. We observe first a yellow spark, which is of the same thickness and which can be seen isolated in narrow tubes. The rotating mirror shows that the discharge is discontinuous. The spectrum consists of bands. Its thickness is much less than that of strong discharges of the Leyden jar which give line-spectra.

In wide tubes we see discharges going out from the positive electrode which are of a red colour. They look like branches of a tree, and appear to be about as thick as a thread. The spectrum consists of bands.

All this shows that the supposition cannot be true which assumes that the band-spectrum is only given out by thick layers, and that it is produced by a superposition of light of feeble intensity and absorption in the gas itself.

Wüllner's hypothesis on the production of band- and line-spectra cannot, therefore, be maintained.

A few objections, and the proof that for some gases Wüllner's propositions can *à priori* be shown to be untenable, must be deferred to another occasion.

Wüllner assumes in nearly all his papers that certain changes in the spectra are produced by certain changes in the pressure. Although he believes the pressure at which these changes take place to be different according to whether it is the simple current of the induction-coil that passes through the gas or the discharge of the Leyden jar, yet these pressures are given as constant quantities for the same mode of discharge and the same chemical composition of the gas. I cannot here refer to the literature upon this subject, but merely give my experiments.

I constructed a tube, one end of which was closed hermetically by a caoutchouc stopper and mercury joint. A knitting-needle was inserted in the stopper and used as electrode, which could be approached to and removed from the second electrode, which was fixed. When the two electrodes were near together the band-spectrum was seen. As the distance increased, the band-spectrum became more feeble, and at last the line-spectrum appeared. As I brought the two needles together again, the same phenomena were seen in the inverse order.

As already mentioned, the spark discharge with line-spectrum has sometimes a little reddish point, the spectrum of which consists of bands.

It is found sometimes that a tube shows a band-spectrum if the spark passes in one direction, and a line-spectrum if it passes in the other.

With discharges of jars the resistances can be so arranged that in rarefied air the sparks just give a band-spectrum while

the jar is charged by an induction-coil the current-intensities of which are variable according to the quicker or slower action of its current-break. If the band-spectrum was just obtained with a quick vibration of the hammer, it sufficed to force this to slower action by increasing its weight, in order immediately to change the spectrum into that of the second order. If the (small) density of a narrow tube which yields a band-spectrum even with jar-discharges is left constant, and the exterior spark-distance of the inserted jar is increased, the band-spectrum can be converted into one which is composed of spectra of both orders, and finally into the pure line-spectrum. The influence of the change in the current-intensity can be controlled in a striking manner, if the density is kept constant, by the enlargements of the hydrogen-lines; in a tube consisting of parts of different widths the hydrogen-lines in jar-discharges are all the more enlarged the narrower that part of the tube is which surrounds the gas. In one and the same part of the tube the lines are the broader the greater the distance in air is which is inserted in the arc. If the same current passes through several tubes of different (but also constant) density, the lines are broader in a very narrow tube with strongly rarefied gas than in a wider one with gas of relatively high density.

If into the current which enlarges the line of hydrogen a moist thread be inserted, the breadth of the lines gets smaller; and by sufficient length of the thread they are restored to perfect sharpness.

With certain low pressures and in certain experiments the lines of pure hydrogen, in spite of large spark-distances inserted, were yet only very little enlarged by jar-discharges. It was to be proved whether in reality there are limits of density beyond which a change of the spectrum is no longer caused by temperature.

As with the use of moist air for discharges of the simple induction-current the lines of hydrogen appear simultaneously with the bands of nitrogen, this indicates a heat of the continuous discharge of the latter which equals the spark-temperature of hydrogen. It was therefore to be expected that, from the strong discharge of sparks with line-spectrum in nitrogen, a heat would result far surpassing the spark-temperature of the former gas; and the *ignition of hydrogen in the nitrogen spark* necessarily exposed it to far higher temperatures and their effects than the spark-discharge in pure hydrogen itself.

In reality the lines of hydrogen which was mixed with nitrogen were far more dim than those of the pure gas at the same pressure.

If to a constant quantity of hydrogen air was admitted, so that the partial pressure remained constant, then its lines grew broader.

Experiments having an exterior similarity to those just described were made by Stearn and Lee, and were described in the Philosophical Magazine for 1873 (vol. xl. p. 406). But while the leading thought of the authors, which they believe finally verified by their experiments, is that the cause of the enlargement of lines depends only on the tension of electricity which passes at a given moment—therefore only on the absolute amount of the total resistance in the closing-arc,—my experiments resulted from the supposition that the above idea was wrong; and this I believe they prove. With an equal total of resistances the jar gives much stronger enlargements when air, as carrying the greatest resistance, is mixed with the hydrogen, than when the spark of the tube passes through pure hydrogen and the greatest resistance in the shape of air is placed outside. In this way I have obtained with a single jar still considerable dimness of the lines with partial pressures in the hydrogen of less than  $\frac{1}{100}$  millim. Pure hydrogen of such minimal density offers insuperable resistance to the currents of induction-apparatus hitherto constructed; in the above experiments, therefore, the nitrogen, which gives a bright spectrum, must not be regarded as a supplementary arc-closer, but as the sole conductor, through which the hydrogen present is only heated.

I conclude from the experiments that any required state of the spectrum can be obtained at any density, however small, if only the gas be exposed to a sufficiently high temperature.

Wüllner has described in detail the constitution of a series of gas-spectra. On account of the theoretical importance which the discoverer attaches to a number of his results, I may be permitted to enumerate here a few differing data, first of all for hydrogen. According to Wüllner, the spectrum of the enlarged lines, and the continuous spectrum resulting from this by raising the temperature, stretches from  $H\alpha$  to  $H\gamma$ , and ends suddenly at the latter line, which is somewhat enlarged. A further extension of the spectrum with further increase of the density of the gas Wüllner even thinks improbable. I have seen very distinctly  $H\delta$ , which Wüllner only mentions in the historical introduction. This line, situated *beyond*  $H\gamma$ , is the first one which enlarges at increasing density or temperature. Between  $H\alpha$  and  $H\delta$  and beyond the latter line a perfectly distinct and quite continuous spectrum appears when the enlargements are not yet at all strong, perhaps corresponding at its most refrangible end to the enlargement-limit of  $H\delta$ , although theoretically there is no sufficient reason for this supposition. In any case the spectrum

extends much further at temperatures not particularly high than Wüllner indicates for the state of perfect formation of the continuous spectrum.

The first spectrum of hydrogen, according to Wüllner, ends between  $H\beta$  and  $H\gamma$ . I have seen it much further. The strong fluorescence of the glass tubes which the light causes ought to have shown long ago that the spectrum is much longer than has been indicated hitherto. The dispersion of brightness in the continuous ground of many line-spectra seems to me to correspond so much with the relative intensity of certain places in the spectrum of the first order, that I tried to get at a continuous spectrum directly from a band-spectrum by raising the temperature. In this I have succeeded very well with nitrogen; unfortunately at present there is no time for a closer investigation of hydrogen in this regard. I do not attach particular importance to a single experiment which confirms my view.

The spectrum of the second order is obtained with the lowest densities in which jar-discharges still go through a narrow tube filled with air; these densities are represented by fractions of a millimetre. If, then, while constantly using jar-discharges one lets the density *increase*, the lines disappear and the band-spectrum appears. If the density still increases, then the brightness of the dimmer band-parts grows perceptibly faster than that of the stronger maxima; the proportion of brightness reaches unity as a limit, and successively more and more bands are replaced by evenly illuminated continuous bright parts. I could extend the continuous spectrum (in which the eye, in spite of great brightness of the whole, does not distinguish any single bands) from the red to the violet; only the most extreme bands at the refrangible end were still distinct. As the formation of continuity progressed in the direction towards the refrangible end, I do not doubt that, with a still more favourable arrangement, even the most extreme part of the spectrum could be obtained perfectly continuous. The absolute brightness of the continuous spectrum was not so great that a deception caused by excessive intensity of light was possible. If the density be then further increased, the line-spectrum again appears on a ground which is already continuously illuminated.

I have convinced myself that the phenomenon I have described has no relation to fluorescence.

The discharge obtains a characteristic colour when the continuous spectrum appears. While it is white for the line-spectrum, rose-coloured for the spectrum of the first order, the light becomes of a yellowish rosy tint as soon as the continuous spectrum appears; so that the eye notices the phase in question without spectral apparatus, by mere observation of the tube.

Some pages back I have spoken of a yellowish rosy part in the negative half of many jars' sparks, which part gives a spectrum continuous as far as the blue: the preceding lines might contain an explanation of this phenomenon (at least with regard to the spectral peculiarity). The outside appearance of it, that in the spark there is a place of different colour and brightness, is already known in principle by observations of machine-sparks by Adams, Knoch, Dove, and others. I have seen similar phenomena with induction-sparks in dense air.

The spectrum of the blue light at the cathode has often been discussed; upon another occasion I will communicate my experiences in respect to this. Here I would only like to draw attention to the fact that colour and spectrum of this light are not always identical. The changes mentioned are most striking when the negative light appears with the optical properties of the positive one. With high rarefaction the negative layers situated from the second towards the outside adopt the colour and spectrum of the positive light.

With jar-discharges of greater intensity the total light near the cathode cannot be distinguished, either by its colour or by the prism, from that of the positive current. The tendency to conform itself to the magnetic curves is then still evident. But negative light can also appear far from the cathode. If tubes like those used for spectral purposes, or many brought into trade as effective articles, cylinders, balls, ellipsoids, are parted off, then each one of these parts behaves during the discharge very nearly like an independent tube having its electrodes at the two entrance-points of the current. At the negative entrance-point light shows itself, which by its straight-lined dispersion, the capacity to cause fluorescence, and the property of conforming itself to the magnetic curves under the influence of a magnet is characterized as negative light. Its form corresponds to that light which would proceed from a cathode, the surface of which would fill the entrance-point. The diffused cloud of light which forms round such an electrode, which has more or less the shape of a point, is represented with the newly found appearance of negative light, by light almost of the colour of the positive. In its spectrum, which on the whole coincides with that of positive light, some maxima of the negative light seem certainly to be marked sharper than the corresponding wave-lengths of positive light. To that cone which, distinguished by brightness, stands perpendicular on the cathode and forms the central axis of the phenomenon, here again a cone corresponds of the colour of the negative light.

I retain the details of this and other, simultaneous phenomena for a future communication.

XXXIX. *On Unitation.*—III. *The Unitates of Powers and Roots.*  
By W. H. WALENN, *Mem. Phys. Soc.*\*

IN former papers† it has been shown that if  $a, b, c, \dots s, t, u$  be the digits of a given number, and  $\delta$  be any integer less than 10,  $n$  being the number of digits in the same number, the expression

$$(10-\delta)^{n-1}a + (10-\delta)^{n-2}b + (10-\delta)^{n-3}c + \dots + (10-\delta)^2s \\ + (10-\delta)t + u$$

has the same remainder to  $\delta$  as the given number has.

By simple substitution of  $\delta$  in this expression, the remainder to  $\delta$  may be found, two kinds of operation being necessary for that purpose. The first is the determination of the coefficients  $(10-\delta)^{n-1}, (10-\delta)^{n-2}, \&c.$ , multiplying each digit by its coefficient and adding the terms thus produced. The second is a repetition of this process such a number of times as will produce a single digit.

This method of obtaining the remainder to  $\delta$  is called *unitation*. The remainder corresponding to a given number for a certain value of  $\delta$  is said to be the *unitate* of the number, and the divisor ( $\delta$ ) the *base* of the system of unitates under consideration. The symbol  $U_{\delta}x$  is used to signify the unitate of the number  $x$  to the base  $\delta$ .

The principles brought to bear, and the examples given in the former papers upon this arithmetical process, showed that it was useful to check calculations, to obtain remainders to a given divisor without the use of any multiple of that divisor, and to verify tables. It was further shown that negative and positive integers could be found, by the process of unitation, to represent unitates that could not be obtained by division.

The nature of the operation of unitation, and its position amongst other operations, will first receive attention, as introductory to the determination of the unitates of powers and roots and to the discussion of some of their properties.

Of the two kinds of operation (necessary for the complete unitation of a number) mentioned above, the first part (involving the addition of terms) is analogous to the formation of an ordinary number, in the decimal system say, another multiplier besides 10 being used; the second operation is analogous to that indicated by the symbol  $\Delta^n$  in the Calculus of Finite Differences, or to that of derivation or successive differentiation indicated by the symbol  $\phi^{(n)}$ . Unitates, however, do not bear

\* Communicated by the Author.

† Phil. Mag. S. 4. vol. xxxvi. p. 346, and vol. xlv. p. 36; and British Association Report for 1870, Transactions of the Sections, p. 16.

upon themselves any symbol to show the number of times that the operation is repeated to produce the result. This indication might be useful in certain instances; and the results of it have yet to be worked out.

Comparing the two methods at present known by which the remainders to a given divisor can be obtained, namely the operation of division and that of unitation, it will easily be perceived that obtaining remainders by division is an inverse process, whereas unitation is a direct process. Division has to be worked out by commencing with the highest or left-hand figure, and proceeding towards the smallest or right-hand figure. Unitation is begun at the right-hand figure and proceeds towards the left-hand figure. In unitating to the base 10, for instance, the unit figure is identical with the unitate; for all the powers of  $(10-\delta)$ , and therefore the coefficients of all the terms containing that factor, become  $=0$ .

These remarks respecting the operation of unitation do not relate in any way to the best and shortest method of obtaining the unitate of a given number to a given base. This was to some extent elucidated in the first article\* upon the subject, in which it was shown to be sometimes advantageous to commence at the left hand and reduce the work as soon as possible. For the purposes of investigation, it may frequently be desirable to retain the coefficients in the same form as the expression cited in the commencement of this article furnishes them, and to proceed with the operation as there indicated†. In practice, when necessary, the coefficients themselves may be unitated to the base  $\delta$ ; this either produces recurring series as coefficients, or else cancels them together with the terms to which they belong. The right-hand figure being the coefficient of the unit belonging to the given number, the following are the series for some values of  $\delta$  :—

$$\begin{aligned}
 \delta = 6 & \dots \cdot, \cdot, \cdot, \cdot, 4, 4, 4, 1 \\
 = 7 & \dots \cdot, 1, 5, 4, 6, 2, 3, 1 \\
 = 8 & \dots \cdot, \cdot, \cdot, \cdot, \cdot, 4, 2, 1 \\
 = 9 & \dots \cdot, \cdot, 1, 1, 1, 1, 1, 1 \\
 = 10 & \dots \cdot, \cdot, \cdot, \cdot, \cdot, \cdot, \cdot, 1 \\
 = 11 & \dots \cdot, \cdot, \cdot, 1, -1, 1, -1, 1 \\
 = 12 & \dots \cdot, \cdot, -8, 4, -8, 4, -2, 1 \\
 = 13 & \dots \cdot, \cdot, -9, 3, -1, 9, -3, 1
 \end{aligned}$$

Unquestionably the most useful and practical of all the systems of unitates included in the above formula (for checking

\* Phil. Mag. S. 4. vol. xxxvi. p. 346.

† For example, in the function  $U_7x$ , the above formula or expression becomes

$$\begin{aligned}
 3^{n-1}a + 3^{n-2}b + 3^{n-3}c + \dots + 19,683l + 6561m + 2187n + 729o + 243p \\
 + 81q + 27r + 9s + 3t + u.
 \end{aligned}$$

calculations and other ordinary purposes) is that which has 9 for its base. Examples and elucidations of this system, and of its applications to arithmetical work, far beyond what has been realized of it as simply "casting out the nines," have been given in the first two papers on the subject. Its peculiarity is that, all the coefficients being unity, every digit of a given number becomes a datum to obtain the result with the simplest possible arithmetical work, namely addition. By a legitimate extension of the meaning of the word unitate, values of  $\delta$  such as 99, 999, &c. come under the same category as  $\delta=9$ ; for instance, the addition of alternate digits gives the unitate of a number to the base 99, and so on.

Taking 2, 4, 5, 8, and 10 as values of  $\delta$ , they would seem to be useless and without any application whatever, since they only include a limited number of terms, and do not necessarily involve all the figures of the given number: this is not the case, however; for 10 (and its congeners 100, 1000, &c.), for example, promise to become most useful for certain purposes. These are the only systems of unitation which give digits in the number itself; and they furnish the means of verifying the last figure, or figures, that the table of logarithms used falls short of, and for other purposes that will hereinafter be more particularly described.

In a theoretical point of view, perhaps the most perfect of any system of unitates (when  $\delta$  is less than 10) is that having the base 7; this system has the greatest number of whole number unitates that it is possible for any base to have. The only other system which will be particularly noticed here is that with the base 11. The unitates to this base are obtained with nearly equal facility to those with the base 9; they are useful as an additional check to calculations; and they possess some properties in common with the function  $U_7x$ .

By taking the ordinary form of the multiplication table, as sometimes put forward in books, so as to form a square\*, as a model upon which to construct a table of the unitates of powers, the advantage is presented of having two series of numbers, one at right angles to the other, open to inspection at a glance, one of the series (the vertical lines) recurring in a number of terms *equal* to the value of  $\delta$ , the horizontal series recurring in a number of terms *dependent upon* the value of  $\delta$ . The following are three of these arrangements (which in respect to the unitates of powers, or to powers at all, are believed to be new), showing the form of each series of unitates of powers, and at the same time that of the series of unitates of powers to the same number †:—

\* See article "Arithmetic" in *Encyclopædia Metropolitana*, by the Rev. George Peacock, D.D., p. 486.

† The square showing the function  $U_\delta a^n$  was given in the paper upon Negative and Fractional Unitates.



## Unitates of Powers to base 7.

	$a^{-2}$	$a^{-1}$	$a^0$	$a^1$	$a^2$	$a^3$	$a^4$	$a^5$	$a^6$	$a^7$
$1^n$	1	1	1	1	1	1	1	1	1	1
$2^n$	2	4	1	2	4	1	2	4	1	2
$3^n$	4	5	1	3	2	6	4	5	1	3
$4^n$	4	2	1	4	2	1	4	2	1	4
$5^n$	2	3	1	5	4	6	2	3	1	5
$6^n$	1	6	1	6	1	6	1	6	1	6
$7^n$	$\frac{1}{7}$	$\frac{1}{7}$	1	7	7	7	7	7	7	7

## Unitates of Powers to base 10.

	$a^{-2}$	$a^{-1}$	$a^0$	$a^1$	$a^2$	$a^3$	$a^4$	$a^5$
$1^n$	1	1	1	1	1	1	1	1
$2^n$	$\frac{1}{2}$	$\frac{1}{2}$	1	2	4	8	6	2
$3^n$	9	7	1	3	9	7	1	3
$4^n$	$\frac{1}{8}$	$\frac{1}{2}$	1	4	6	4	6	4
$5^n$	$\frac{1}{5}$	$\frac{1}{5}$	1	5	5	5	5	5
$6^n$	$\frac{1}{8}$	$\frac{1}{8}$	1	6	6	6	6	6
$7^n$	9	3	1	7	9	3	1	7
$8^n$	$\frac{1}{2}$	$\frac{1}{8}$	1	8	4	2	6	8
$9^n$	1	9	1	9	1	9	1	9
$10^n$	$\frac{1}{10}$	$\frac{1}{10}$	1	10	10	10	10	10

## Unitates of Powers to base 11.

	$a^{-2}$	$a^{-1}$	$a^0$	$a^1$	$a^2$	$a^3$	$a^4$	$a^5$	$a^6$	$a^7$	$a^8$	$a^9$	$a^{10}$	$a^{11}$
$1^n$	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$2^n$	3	6	1	2	4	8	5	10	9	7	3	6	1	2
$3^n$	5	4	1	3	9	5	4	1	3	9	5	4	1	3
$4^n$	9	3	1	4	5	9	3	1	4	5	9	3	1	4
$5^n$	4	9	1	5	3	4	9	1	5	3	4	9	1	5
$6^n$	4	2	1	6	3	7	9	10	5	8	4	2	1	6
$7^n$	9	8	1	7	5	2	3	10	4	6	9	8	1	7
$8^n$	5	7	1	8	9	6	4	10	3	2	5	7	1	8
$9^n$	3	5	1	9	4	3	5	1	9	4	3	5	1	9
$10^n$	1	10	1	10	1	10	1	10	1	10	1	10	1	10
$11^n$	$\frac{1}{11}$	$\frac{1}{11}$	1	11	11	11	11	11	11	11	11	11	11	11

The double vertical lines in the above diagrams show the period of recurrence in the unitates of the positive powers of a given number; this, in the function  $U_7 a^n$ , is 6 terms, in  $U_{10} a^n$ , 4 terms, and in  $U_{11} a^n$ , 10 terms. The Table in the margin gives the periods of recurrence for the values of  $\delta$  up to 10, P being the corresponding period. In the above "unitation squares," the series of unitates is continued towards the left hand to show the law of formation of  $U_\delta a^{-n}$ , which in some cases is different from that of  $U_\delta a^{+n}$ . By means of these unitation squares, the unitate of any power of any number to the given base may be calculated by inspection, knowing the recurring figures and the period of recurrence; for instance,

$\delta$ .	P.
2	1
3	2
4	2
5	4
6	9
7	6
8	2
9	6
10	4

$$U_9 43^{562} = U_9 7^4 = 7; \quad U_7 256^{647} = U_7 4^5 = 2;$$

$$U_{11} \frac{1}{5217^{6345}} = U_{11} 3^{-5} = 1.$$

Practically there is not much difficulty in finding  $U_\delta \sqrt[m]{q}$  when it is finite or integral; for it may be ascertained from the root itself (by extraction), or from looking out  $U_\delta q$  in the table of unitates belonging to the series  $U_\delta a^m$  and ascertaining the corresponding value of  $U_\delta a$ . It will, however, sometimes be found that there are several values of  $U_\delta a$  that will fulfil the conditions; for instance,  $U_9 \sqrt[3]{729} = U_9 \sqrt[3]{9}$ ; and, looking for 9 in the series 1, 8, 9, 1, 8, 9, 1, 8, 9, ..., it is seen to belong to 3, 6, or  $9^*$ ; a method of ascertaining the true unitate by means of a unitation square will be given further on. It will be discovered upon examination that in unitates, as in some other numerical results, there may be  $m$ th roots,  $n$ th roots, and so on.

Considering unitates as remainders, and inspecting the series of unitates in unitation squares, it will be evident that the unitates of some surd roots have finite and integral values. These values may be determined in the same manner as the unitates of rational roots; for instance, from the series  $U_9 a^2 (= 1, 4, 9, 7, 7, 9, 4, 1, 9, \dots)$ ,  $U_9 \sqrt{7} = 4$  or 5. Further, it will be found, from these reasons, that  $U_\delta \sqrt[m]{q}$  ( $m$  and  $q$  being whole numbers, and  $\sqrt[m]{q}$  being irrational) is finite and integral when  $\delta$  is of the form  $n^m - q$ ; in this case  $n$  is any whole number excepting unity, taking care to choose  $n$  so large that the expression  $n^m - q$  may not be negative.

Unitation squares, formed in geometrical progression with respect to exponents (in the horizontal series), may be used to obtain the unitates of certain roots, the base of the system being

$$* U_{11} \sqrt[3]{729} = U_{11} \sqrt[3]{3} = 9.$$

determined by the expression  $\delta = n^m - q$ , as above stated. The following are some of the series that may be used :—

$$a^{\frac{1}{16}}, a^{\frac{1}{8}}, a^{\frac{1}{4}}, a^{\frac{1}{2}}, a^1, a^2, a^4, a^8; \quad a^{\frac{1}{27}}, a^{\frac{1}{9}}, a^{\frac{1}{3}}, a^1, a^3, a^9, a^{27}, a^{81}; \\ a^{\frac{1}{125}}, a^{\frac{1}{25}}, a^{\frac{1}{5}}, a^1, a^5, a^{25}, a^{125}, a^{625}.$$

Thus  $U_7 \sqrt{2} = 3$  or 4.

Taking the leading principle of the function  $U_{10^n} x$  as true when  $x = \sqrt[m]{q}$  (an irrational quantity)—an extension that must not be made without realizing the extent of the step involved in it (namely, that the extreme right-hand figure or figures is or are given by this class of unitates)—it would seem possible to assign a value to the last figures of some incommensurable quantities; it would appear, for instance, that  $U_{10} \sqrt{5}$  must be 5. If this be true, the real *terra incognita* of incommensurable quantities does not always lie at their extreme right-hand end, but in the middle region of their interminable decimal. This supposition would make good an analogy between the curves to certain equations (namely those that have a curve of finite perimeter at an infinite distance from the origin) and certain incommensurable quantities. Although the subject must be dealt with very cautiously, there does not seem any incongruity in the conception; and the range of thought thus opened to the mind is new.

The points brought forward in this paper have been verified and tested by inductive reasoning, by the laws of their existence, and by examples, according to the methods more particularly set forth in the last paper—that upon negative and fractional unitates.

The foregoing remarks and elucidation show that unitation is not identical with any known process. As an operation it is a direct process, dependent upon repetition for its completion. A unitate is a function which, in some of its results, gives a finite and integral value when applied to quantities that are neither finite nor integral.

The further the investigation of unitation proceeds, the more unitates manifest themselves as functions that may be found throughout all the domain of quantity, and as, in some instances, interpretable when the quantity from which they are derived is but imperfectly known.

74 Brecknock Road, N.,  
March 1875.

XL. *Researches in Acoustics.* By ALFRED M. MAYER\*.—No. VI.

[Continued from vol. xlviii. p. 525.]

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“Consonanz ist eine continuirliche, Dissonanz eine intermittirende Tonempfindung.”—Helmholtz.

1. *The Determination of the Law connecting the Pitch of a Sound with the Duration of its Residual Sensation.*

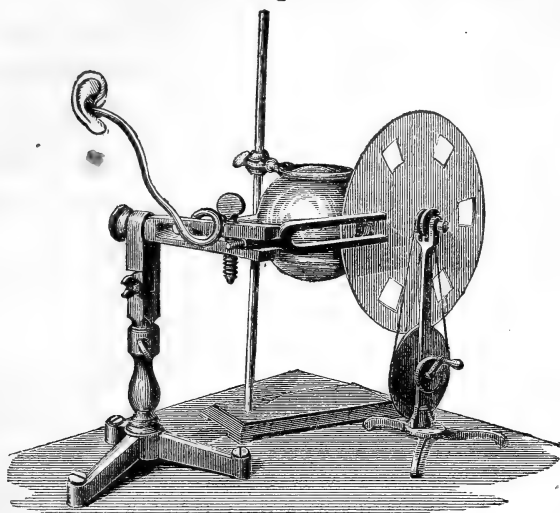
WHILE the durations of the residual sensations on the eye, corresponding to lights of various colours and intensities, have been the subjects of many masterly memoirs, I know of no attempts to determine the durations of the residual sonorous sensations. Helmholtz founds indeed his Physiological Theory of Music on the facts that a certain number of beats per second produce in the ear a maximum dissonant sensation, while a greater number may blend into a smooth continuous sound; and in discussing the position in his scale of the “damping-powers” of the covibrating parts of the organ of Corti, Helmholtz (*Tonempf.* p. 212 *et seq.*) infers, from the difficulty of trilling on the bass notes, that the covibrating parts of the ear set in motion by sounds of low pitch maintain their vibrations longer than those excited by sounds belonging to higher portions of the musical scale. He says:—“Trills of this kind, of ten notes per second, are of a sharp and clear execution in the greatest portion of the musical scale; below the *la* of 110 vibrations in the grand and contra octaves, however, they sound bad, harsh, and the sounds begin to blend.” Yet it does not appear that Helmholtz ever attempted to determine that *quantitative relation* existing between the pitch of a sound and the duration of its residual sensation which I will now endeavour to establish. This law in its further applications will render quantitative many of the qualitative statements contained in Helmholtz’s renowned work.

The method of obtaining the facts (of which our law expresses the general relation) is similar to the method used in the study of the analogical phenomena of light. A simple sound was obtained by vibrating a fork before the mouth of its corresponding resonator; and this sound was broken up into flashes, or explosions by alternately screening and unscreening the mouth of the

\* Communicated by the Author.

resonator, by means of a perforated disk which rotated between the resonator and the fork, as is shown in the accompanying fig 1.

Fig. 1.



The mean diameter of the open sectors of the disk equalled the diameter of the mouth of the resonator, while the spaces of cardboard between the open sectors was twice the width of these openings. Thus the resonator's mouth was exposed to the vibrations during an interval which equalled that during which it was screened from them. A rubber tube led from the nipple of the resonator to one ear, while the other ear was tightly closed with a lump of bees-wax.

In my first experiment I firmly clamped an  $Ut_2$  resonator, and vibrated opposite its mouth an  $Ut_2$  fork. I now placed the tube in the ear, and on slowly rotating the disk I perceived a series of sharply separated explosions or beats. On gradually increasing the velocity of the disk these explosions gradually approached each other; and on reaching a certain frequency in their succession they blended into a continuous smooth sensation, similar to that experienced when the disk was removed and the fork vibrated gently before the resonator. I now kept the disk at the velocity required just to blend the separate beats; and I found, on timing its rotations, that the resonator was sending into my ear about thirty explosions or beats per second. Hence sonorous waves of  $Ut_2$  cut into thirty parts per second, or, in other words, divided into lengths of about four waves separated by the same lengths of quiescence, produce the same sensation as that caused by an uninterrupted flow of these sonorous waves into the

ear. I now replaced the  $Ut_2$  resonator and fork by an  $Ut_4$  resonator and its corresponding fork, and again rotated the disk with the same velocity that it had during the above-described experiment. In these circumstances I no longer experienced a continuous sensation, but one which reminded me somewhat of the clatter of frogs in a marsh. This fact at once showed that a greater number of beats per second were required to blend the separated pulses of a sound of higher pitch; and this blending I actually obtained on sending into my ear about one hundred beats per second of  $Ut_4$ .

I now prepared a series of disks adapted to four octaves of resonators and forks, and made many experiments to determine the durations of the residual sonorous sensations of several simple sounds— $Ut_1$  of 64 vibrations per second being the lowest note of the series, and the highest being  $Ut_5$  of 1024 vibrations. I was not able to use an  $Ut_1$  fork and resonator; so I substituted for the former an  $Ut_1$  closed wooden organ-pipe, gently blown, and for the latter a small funnel of gutta percha, whose mouth was placed close to the perforated disk, while a rubber tube connected the funnel with the ear. I will here remark that in some series of experiments the resonators were replaced by this funnel of gutta percha, and the determinations thus made were the same as those reached by the use of the resonators.

The above-mentioned determinations I published in the *American Journal of Science* for October 1874, and embraced them in a law which has for its expression  $D = \left( \frac{53248}{N + 23} + 24 \right) \cdot 0001$ , in

which  $D$  equals the duration of the residual sonorous sensation corresponding to  $N$  number of vibrations per second.

The precise determinations of the durations of the residual sonorous sensations are difficult, by reason of the complex character of the sound perceived when vibrations of a tuning-fork are sent intermittently into a resonator by means of a revolving perforated disk; and the difficulty of the determinations is increased by the fatigue and deadening of the ear, caused by the beats which enter it from the resonator.

The important applications of this law in the physiology of audition and in the elucidation of the fundamental facts of musical harmony, demanded that I should have my determinations reviewed by ears more highly cultivated than mine in the appreciation of pitch and of musical intervals, and more skilled in the direct oral analysis of composite sounds into their simple tones. Since my publication in October 1874, I have had the good fortune to elicit in Madame Emma Seiler, and in her son Dr. Carl Seiler, a profound interest in my researches. They have spent considerable time in the redetermination of the dura-

tions of the residual sonorous sensations, making use, under my directions, of the same apparatus which I employed in my original experiments. Madame Seiler in former years worked much with Helmholtz, assisting him with her fine ear in experiments contained in his renowned work *Die Lehre von den Tonempfindungen*. This lady unites to educated musical perceptions a knowledge and appreciation of recent advances in physiological acoustics; and hence I have great confidence in the determinations made by her. These results I give in the following Table, which I desire to take the place of that published in my paper of October 1874.

Column S of this Table contains the simple sounds experimented on; they are designated in the notation stamped by König on his forks. Column N gives the number of vibrations\* per second corresponding to the sounds of column S. In column D are the corresponding durations of the residual sensations, expressed in vulgar and in decimal fractions. The reciprocal of the number of beats per second required to produce a continuous sensation by a given sound is taken as the duration of the residual sensation of this sound†. In column L are given the number of wave-lengths contained in the separate impulses into which the sound had been divided in order to produce the continuous sensation.

S.	N.	D.	L.
Ut <sub>1</sub> .	64	$\frac{1}{25} = \cdot 0395$ sec.	2·5
Ut <sub>2</sub> .	128	$\frac{1}{45} = \cdot 0222$ „	2·8
Ut <sub>3</sub> .	256	$\frac{1}{70} = \cdot 0142$ „	3·6
Sol <sub>3</sub> .	384	$\frac{1}{102} = \cdot 0098$ „	3·7
Ut <sub>4</sub> .	512	$\frac{1}{180} = \cdot 0076$ „	3·9
Mi <sub>4</sub> .	640	$\frac{1}{152} = \cdot 0065$ „	4·1
Sol <sub>4</sub> .	768	$\frac{1}{188} = \cdot 0060$ „	4·6
Ut <sub>5</sub> .	1024	$\frac{1}{180} = \cdot 0055$ „	5·6

Although at first sight the apparatus which I have used in this research may appear coarse, yet experience showed that the accuracy of a determination depended more on the ear than on

\* I here, as always, refer to complete vibrations, *i. e.* to a motion to and fro, or to what the late Professor De Morgan proposed to call a *swing-swang*.

† That is to say, we take as the duration of the residual sensation the interval during which the impress of a beat has not diminished sufficiently in intensity to cause discontinuity in the sensation. To obtain the duration of the entire sensation, we should have to know the intensity of the sensation at the end of the above interval, and the law giving the rate of diminution of the sensation.

the mechanical appliances of our experiments; for the average difference in the measures of the duration of any one residual sensation did not exceed the  $\frac{1}{4000}$  of a second. The perforated disk made  $3\frac{3}{4}$  revolutions to one of the driving-crank; and if the disk has twelve perforations, then the above difference of  $\frac{1}{4000}$  of a second is given by the difference between two observations, in one of which the driving-crank made 30 revolutions in ten seconds, and in the other made 29 revolutions in the same time. It is evident that the apparatus readily detects this difference, especially as I often ran it during thirty seconds to obtain the number of beats striking the ear during one second.

Before accepting as final the above determinations, I ascertained that great differences in the intensities of the pulses had little effect on the number of beats required to produce a continuous sensation. When a great increase in intensity was given to the pulses, their number had to be slightly increased to produce the same continuous sensation as that experienced with feebler pulses; but the difference was barely measurable. It is also important to remark that, after the blending of the pulses has been once attained, a further increase in the velocity of the disk does not change the character of the sensation. Extreme velocities, of course, produce such violent agitations at the mouth of the resonator as to render experimenting impossible.

I have projected the above determinations into the accompanying curve (fig. 2), placing on the axis of abscissæ the numbers of vibrations of the various sounds, as designated at the base of the figure, and on the ordinates the corresponding durations of their residual sensations. Thus has been obtained the full-lined curve of the figure. The dotted curve is an equilateral hyperbola, and expresses an assumed law—that the durations of the residual sensations are inversely as the numbers of vibrations producing them. In drawing the latter curve, I took the point corresponding to the ordinate of  $U_3$  as the basis of the assumption.

From the discussion of the curve of the experiments, we find that the law connecting the pitch of a sound with the duration of its residual sensation may be expressed thus,

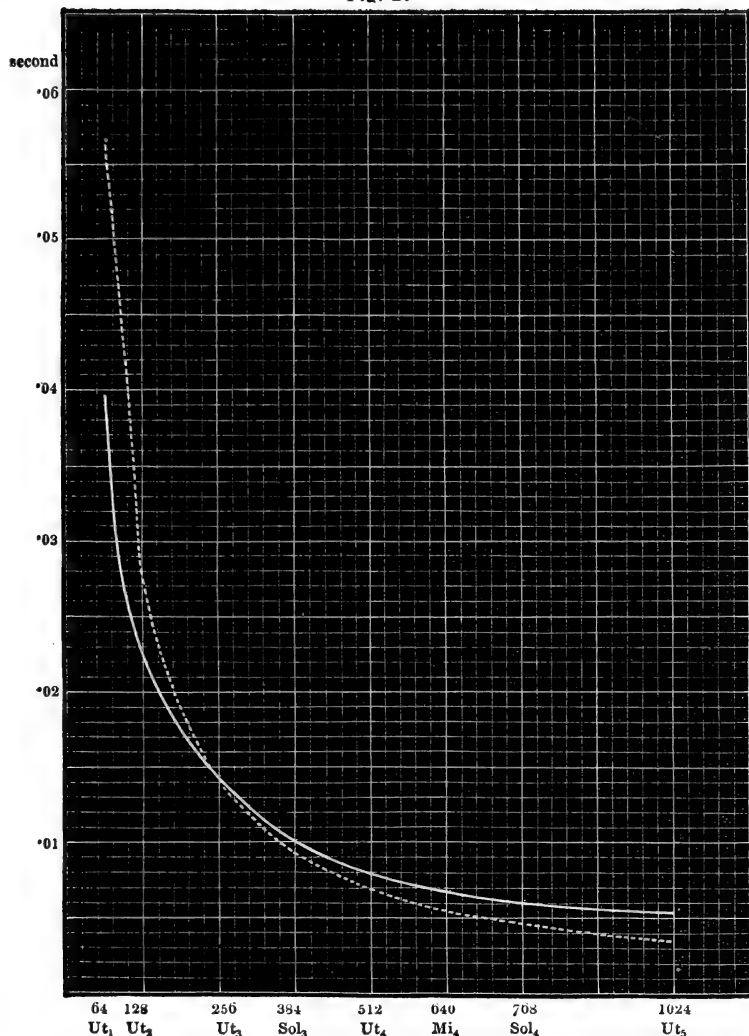
$$D = \frac{3 \cdot 2}{N + 31} + \cdot 0022,$$

in which  $D$  equals, in fractions of a second, the duration of the residual sonorous sensation corresponding to  $N$  number of vibrations per second.

We have already spoken of the difficulty of the determination of the residual sonorous sensations by reason of the complex character of the sound perceived when the vibrations of a tuning-



Fig. 2.



fork are sent intermittently into a resonator by means of a revolving perforated disk. I will now describe the character of the successive sensations experienced when, starting from rest, we gradually increase the velocity of rotation of the disk until the separate beats of the fork blend into a smooth continuous sensation. When the disk is stationary, with one of its openings opposite the mouth of the resonator, it is evident that the ear will

experience a simple sonorous sensation when a tuning-fork is brought near the mouth of the resonator. On revolving the perforated disk, two additional or secondary sounds appear—one slightly above, the other slightly below the pitch of the fork. An increasing velocity of rotation causes the two secondary sounds to diverge yet further from the note of the beating fork, until, on reaching a certain velocity, the two secondary sounds become separated from each other by a major sixth, while at the same moment a resultant sound appears, formed by the union of the sound of the fork with the upper and lower of the secondary sounds. This resultant is the lower second octave of the note given by the fork. On further increasing the velocity of rotation of the disk, the two secondary sounds and the resultant disappear, and the ear experiences only the sensation of the simple sound produced by the fork, whose beats at this stage of the experiment have blended into a smooth continuous sensation. These successive and gradual changes, as they happen with an  $Ut_4$  fork, we have indicated in steps of semitones in the appended musical notation. The sound of the fork is given in the semibreve, while the crotchets represent the secondary sounds and the resultant sound. In the fourth bar the upper note  $bE$  proceeds to  $\sharp D$  in the fifth bar. This is so because in the natural scale  $\sharp D$  is higher than  $bE$ .



## 2. *The Determination of the numbers of Beats, throughout the musical scale, which produce the greatest Dissonances.*

The determination of the law which shows the connexion existing between the pitch of a sound and the number of its beats which causes the most dissonant sensation, was made with the same apparatus that served for the discovery of the law just discussed. The determination of the number of beats producing the greatest dissonant effect with a given sound is difficult; for the point of maximum dissonance is not sharply marked, and individual judgment and peculiarities come in, so that the range of the determination for any given sound, by different persons, is considerable. But on discussing the determinations reached by any one person, I found that they followed a well-marked law, which, as might have been inferred, is closely connected with the law of the duration of the residual sensation. Indeed we find that any one observer always makes the numbers produ-

cing the maximum dissonances a constant fraction of the numbers of beats which give continuous sensations. Thus I find that  $\frac{3}{10}$  of the latter numbers give me the most disagreeable sensations; another observer has placed the fraction as high as  $\frac{1}{60}$ . I imagine that we do not greatly depart from an average judgment in stating that about  $\frac{4}{10}$  of the number of beats, throughout the musical scale, which produce continuous sensations, correspond to the numbers of beats giving the greatest dissonant effects. Thus we can go from the law connecting the pitch of a sound with the duration of its residual sonorous sensation to the law giving the numbers of beats throughout the musical scale which produce the most dissonant sensations.

3. *Application of the above Laws in a new Method of Sonorous Analysis, by means of a perforated rotating disk.*

It is an interesting deduction from the laws we have established that a composite sound can be analyzed by means of a rotating disk with sectors cut out of it. Thus, on rotating a large perforated disk with great velocity before a reed-pipe and placing the ear close to the disk (or in connexion with the gutta-percha funnel, by means of the rubber tube), we shall have the composite sound reaching the ear in a series of impacts which succeed each other so rapidly that even those of the highest harmonic of the reed blend into a continuous sensation; but on gradually lowering the velocity of rotation, the impacts of this highest harmonic can no longer blend, and we perceive the harmonic beating on the ear alone. This can be readily confirmed by the aid of a resonator. A further slight lowering of the velocity brings out the beats of the next lower harmonic, and so on until the velocity has been so diminished that even the beats of the lowest, or fundamental, harmonic are perceived; and then all of the component sounds of the reed are beating in unison; but yet the effects they produce on the ear are very different; for the higher harmonics, notwithstanding their feeble intensities, must be heard more distinctly, because their intermittences are furthest removed from the numbers that cause their sensations to blend. In other words, the highest harmonics, in the phase of the experiment above described, approach nearer than the lower to the numbers of beats required to cause them to give their greatest dissonant effects. This method of sonorous analysis was arrived at as a deduction from our laws; and subsequent experiments confirmed the assumption that a sonorous analysis could be thus effected. This curious discovery has its analogue in the case of light; for when a disk with alternate white and black sectors is rotated so slowly that distinct flashes of white light are perceived, the retina is thrown into states of successive increasing and de-

creasing excitation. Now the moment of the maximum of excitations is not the same for all colours, but the excitation takes place sooner for the red and the violet than for the green. "Si l'on fait tourner un semblable disque, lentement d'abord, puis, graduellement, de plus en plus vite, et qu'on le regarde fixement, en évitant de suivre du regard l'image en mouvement, on remarque que le blanc se colore en rougeâtre sur le bord qui se présente le premier, et en bleuâtre sur le bord postérieur. Pour un faible éclairage, le ton rougeâtre tire plus sur le jaune-rouge, le bleuâtre sur le violet; pour un éclairage intense, le premier tire sur le rose, le second sur le bleu-vert. Si la rotation est lente, le ton bleuâtre s'étend d'abord sur une plus grande partie du blanc que le ton rougeâtre. Si, au contraire, la rotation est rapide, le rouge s'étend en rose sur tout le blanc, tandis que le bleu-vert s'avance sur les secteurs noirs; en somme, le violet paraît alors prédominer sur tout le disque. Pour une rotation encore plus rapide, on ne distingue plus l'un de l'autre les différents secteurs; on voit alors le champ finement jaspé de taches qui papillotent entre le rose-violet et le gris-vert. Enfin, si la rapidité de la rotation augmente encore, le papillotage diminue, la couleur grise résultant du blanc et du noir ressort de mieux en mieux et n'est plus recouverte que par de grandes taches variables, d'un rose violet, qui présentent l'aspect des taches et des bandes qu'on voit sur un tissu de soie mouillé" (Helmholtz, *Optique Physiologique*, Paris, 1867, p. 500).

#### 4. *Deductions from these Laws leading to new Facts in the Physiology of Audition.*

The immediate consideration of the laws we have established gives the most convincing confirmation of Helmholtz's ideas of the high differentiation in the dynamic constitution or mechanism of the ear. The very fact of the ear's power to effect a sonorous analysis was shown by Helmholtz to be a proof of this; but our physiological law, susceptible of a mathematical expression, affords the most direct proof that one could desire of the existence in the ear of a highly differentiated mechanism, so differently affected in its different parts by sounds of different pitch. Indeed Helmholtz also divined this even from his restricted premises, which I have had the privilege of enlarging; for he says (*Tonempf.* p. 215):—"As the difficulty of making a trill in the bass is the same on all musical instruments, and as it is evidently altogether independent of the mode of production of sound on each instrument, we have to conclude that we have here to do with a difficulty which resides in the ear itself. Here is a phenomenon which neatly proves that the vibrations of the mobile parts of the ear for bass sounds are not "damped" sufficiently,

or quickly enough, to prevent two sounds from succeeding each other so rapidly without blending.

"This fact proves, besides, *that there should be in the ear different parts which are set in vibration by sounds of different height, and which give the sensations of these sounds.* Some may imagine that the mass of the vibratile elements of the ear, comprising the tympanic membrane, the ossicles, and the liquid of the internal ear, can vibrate, and that it is on this property of this mass that depends the impossibility of sonorous vibrations ceasing with the same rapidity in the ear. But this hypothesis does not suffice to explain the known facts.

"When, in fact, an elastic body enters into vibration under the influence of an exterior sound, it takes the number of vibrations of the latter; but as soon as the exciting sound ceases, it vibrates with the number of vibrations which belongs to it when vibrating freely. This fact, which is a consequence of theory, can be very neatly proved for tuning-forks by means of the vibration-microscope.

"Therefore, if the ear vibrate as an entire system," and is capable of prolonging notably its vibrations, this prolongation should depend on the number of its own free vibrations, which is altogether independent of the number of vibrations of the exterior sound which excited the vibratory motion. It at once follows that it will be as difficult to trill among the high notes as among those of the bass, and, also, that the two sounds of the trill will blend, not with each other, but with a third sound belonging to the ear itself. We have already made known one of the sounds in the preceding chapter: it is the  $fa_6^*$ . In these circumstances, consequently, the result should be altogether different from that given us by the observation of the facts."

If we extend our law downward and upward, throughout the range of audible sounds, we have for forty vibrations per

\* I here adopt, as I always do, the French notation, which is used by König. Those who use the French translation of Helmholtz's work should be on their guard to observe that the translator has lowered all of his notation one unit below that used in France, and he thus gives all of Helmholtz's notes too low by an octave. Thus the translator's  $Ut_2$  should read  $Ut_3$ .

The fact to which Helmholtz refers above is that the human ear is tuned, by resonance, to the  $fa_6$  of 2730 complete vibrations; so that the vibrations of this note and of those near it cause piercing sensations in our ears. If a short tube be adapted to the external auditory canal, these disagreeable sensations disappear, as the canal can no longer resound to the above note; but the same piercing sensation will now reappear on sounding a lower note. Mad. E. Seiler, now of Philadelphia, has shown that dogs are peculiarly sensitive to the acute *mi* of the violin.

second a residual sensation lasting  $\frac{1}{20}$  of a second; while for 40,000 vibrations per second we have a residual sensation enduring only  $\frac{1}{438}$  of a second. If we apply the law to vibrations below forty per second, when they do not produce a continuous sound, but explosive sensations in the ear, we reach a remarkable result. Thus the residual sensation corresponding to thirty vibrations per second should remain in the ear  $\frac{1}{18}$  of a second after the vibrations outside the ear have ceased; then we at once ask why is it, if the residual sensation lasts  $\frac{1}{1}$  of a second, that thirty beats or pulses per second do not blend? This abrupt breaking down of the law can only be explained by the highly probable supposition that covibrating bodies in the ear, tuned to vibrations below forty per second, do not exist, and therefore, as there are no bodies in the inner ear to covibrate and keep up these oscillations after the cause which would have set them in motion has ceased to exist, it follows that when the ear receives less than forty vibrations per second it can only vibrate *en masse*, and the durations of these oscillations of the ear, as a whole, are far too short to remain the  $\frac{1}{30}$  of a second. The last supposition, as to the vibration of the ear as a mass, may serve to explain why the higher notes (far beyond those used in the musical scale) produce continuous sensations; for, to these very high sounds we can hardly imagine corresponding tuned bodies; yet they produce continuous sensations. But may it not be imagined that the ear with them does also only vibrate as one mass, and that the duration of this vibration is sufficient to give continuous sensations from pulses following at the rate of several thousand per second? But for notes thus perceived (without the intervention of corresponding covibrating parts in the inner ear) differences of pitch should be difficult, even impossible, to distinguish; and this we find to be the case.

The fact that the durations of the residual sensations diminish as the numbers of vibrations producing the sounds increase, leads to the knowledge of a new and curious phenomenon in the physiology of audition, viz. that the timbre of a composite sound begins to change at the instant the vibrations outside the ear have ceased; for from that instant the residual sensation becomes more and more simple in its character, until at last only the simple sound of the fundamental harmonic remains in the ear; and soon after, this sensation also vanishes. Thus, after the vibrations of an  $Ut_2$  reed-pipe containing twenty harmonics have ceased, the residual sensation of the twentieth harmonic, or that highest in pitch, disappears in the  $\frac{1}{291}$  of a second; but the sensation of the fundamental or lowest harmonic remains in the ear  $\frac{1}{33}$  of a second after the

sensation of the highest has vanished; and the fundamental remains  $\frac{1}{126}$  of a second after the cessation of the sensation of the harmonic next above it.

The successive rates of increase of the ordinates of the curve which expresses our law, as we go from the ordinate belonging to the highest note to that belonging to the lowest, represent the rate of successive extinctions of these harmonics in the composite residual sensation. These successive changes in timbre are well illustrated by sounding all the twenty forks of the harmonic series of  $Ut_2$  and then stopping the vibrations successively, going from the highest to the lowest.

The remarkable phenomenon we have just described has also its counterpart in the analogous series of changes in visual sensations which happen when the eye has received the sudden impress of a bright white light and is then immediately closed in darkness. Thus the average duration of the residual sensation in the eye is the  $\frac{1}{24}$  of a second for lights of moderate intensity; but if the image of a bright cloud be received on the eye for  $\frac{1}{3}$  of a second, the "positive sensation" remains for twelve seconds. The duration of this residual sensation depends on the colour—lasting longer for red than for violet, and longer for violet than for green. Here an analogy with our sonorous sensations is presented; for the ætherial vibrations producing red are fewer in number than those producing either green or violet, and the sensation of red lasts longer than either green or violet; and therefore it follows that we should have the residual image of the sun go through these changes—white, greenish-blue, blue, violet, purple, red; and this is what really happens when the sun's image is momentarily formed on the retina, and the eye then kept in darkness.

The above analogy, however, is imperfect if it really is established that the residual sensation of violet lasts longer than that of green when the vibrations giving these two colours have equality of energy. The analogy also is one of *sensations*, not one of the *mechanisms* existing between the agents and the sensations they produce; for, in the case of the ear, anatomical facts give us bases for the explanation of the ear's power of effecting a sonorous analysis, and for the understanding of the reason of our law of the duration of the residual sensation. In other words, in the ear we have laid before us the mechanism (1) of the receiving apparatus, (2) of the transmitting apparatus, and (3) of the sensory apparatus; but in the eye we comprehend only (1) and (2), but we know as yet nothing that gives us an understanding of the dynamics of the sensory apparatus. For has modern histology given us any facts concerning the structure of the human retina which point to the establish-

ment of Young's hypothesis of three distinct sets of retinal nerve-terminations? The more we study the minute structure of the retinal rods and cones, the further appears to remove an understanding of the mode of operation of the sensory apparatus of the eye. May not research in this direction be guided by the hypothesis that the *molecular* constitution of the retinal rods and cones is such that their molecules are severally tuned to the vibrations corresponding to the colours red, green, and violet? This would lead us to look for effects of actinism on the retina as showing the link existing between the transmitting and sensory functions of the eye. Do not the facts of the known persistence of chemical action, after it has been once initiated, and the time which would be required for the retinal molecules to recombine, or rearrange themselves, after the ætherial vibrations had ceased, comport with the known durations of the residual visual sensations, and with the main facts of physiological optics, better than the hypothesis that masses of the retinal elements are set in vibration rather than their molecules?

##### 5. *Quantitative Applications of the Laws to the fundamental facts of Musical Harmony.*

To show the full value of these laws in introducing quantitative precision in the explanations of consonance and dissonance would require an extended space; we here present only such application as will serve to show their importance in giving clear and simple guides in reasonings in the physiological theory of musical harmony.

We have seen that 26 beats of the simple sound  $C_1$ , of 64 vibrations per second, give a continuous sensation; therefore, to determine the nearest consonant interval of this note, we have to obtain a sound which will make with  $C_1$  the vibration-ratio of  $64 : 64 + 26$ . This would show that the nearest consonant interval of  $C_1$ , on the natural scale, is its fourth plus  $\frac{2}{3}$  of a semitone. The duration of the residual sensation of  $Ut_4$  is  $\frac{1}{1.50}$  of a second; hence, to determine by our law the nearest consonant interval of  $Ut_4$ , we must combine with it a note which will give with  $Ut_4$  the vibration-ratio of  $512 : 512 + 130$ . This note is the E above  $C_4$ —that is, its major third. In the following Table we give the determinations of the nearest consonant intervals of the Cs throughout five octaves\* :—

\* We have, for simplicity of illustration, determined the above intervals on the basis of the pitch of the lower note; but as the beats are produced by the conjoined action of the two sounds, it would have been more accurate to have taken, as a second approximation, the mean pitch of the two sounds. Thereby the above determinations would be somewhat changed for lower, but not perceptibly for higher notes.



$C_1$	of	64 vibrations,	interval = fourth	$+\frac{2}{3}$ semitone.
$C_2$	"	128	" = fourth	$+\frac{2}{9}$ "
$C_3$	"	256	" = major third	$+\frac{2}{7}$ "
$C_4$	"	512	" = major third	$+\frac{1}{2\frac{1}{2}}$ "
$C_5$	"	1024	" = minor third	$-\frac{3}{10}$ "
$C_6$	"	2048	" = one tone	$+\frac{1}{15}$ "

We thus see that while in the neighbourhood of  $C_1$  the nearest consonant interval is over a fourth, in the octave of  $C_6$  the nearest consonant interval has contracted to a tone. This result seems to show why it is that the middle portion of the musical scale is best adapted for expression, and is most used in musical composition; for while in the lowest octaves the available consonant intervals are few on account of the extended spaces separating them, in the highest octaves the consonances are so contracted that their highest consonant intervals lose the sharpness of definition given when these are bounded by distinctly marked dissonances.

It is here to be remarked that in our experiments we have obtained continuous and discontinuous sensation from beats produced by one sound of a constant pitch; but with musical intervals we obtain beats from two sounds differing in pitch. In the latter case De Morgan, Guérout, Helmholtz, and Mr. Sedley Taylor have shown that there exists a variation, or oscillation, in pitch whenever the two sounds are not of the same intensity. Mr. Taylor\*, from this fact, advances the idea that these oscillations in pitch cause a *noise* in place of a *sound*, and to this result is due, in great part, the dissonance produced by beats of two different sounds. That oscillations of pitch occur when the two sounds are of unequal intensity is a fact of which there can be no doubt; but that this oscillation of pitch is the principal cause of the dissonant sensations which are perceived when beats occur, my own experiments do not verify; yet I admit that the phenomenon has its effect in increasing slightly the dissonant character of the beats. But even assuming that Mr. Taylor's explanation of the dissonance of beats is correct, yet our views hold good when we regard the intervals as formed of sounds which are equal in intensity.

In concluding this paper, I should call attention to the evident difference existing between the dynamic constitution of the sonorous waves belonging to beating pulses produced by the action of a perforated rotating disk on a continuous stream of sonorous vibrations, and those waves which cause beats and which are formed by the joint action of sonorous vibrations differing in pitch. That these two kinds of beats are alike in their effects when following in the same rapidity I have assumed to be the fact in this paper.

\* "On the Variations of Pitch in Beats," by Sedley Taylor, Esq., Phil. Mag. July 1872.

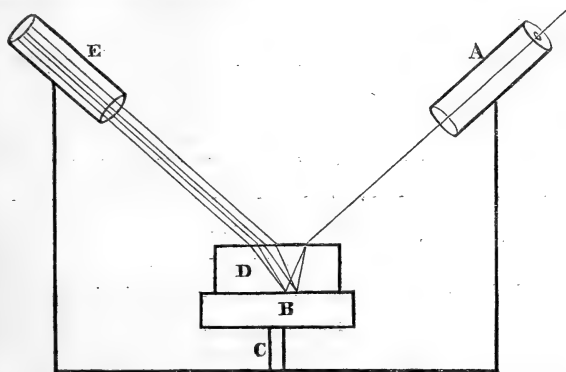
XLI. *On Extraordinary Reflection.* By ARTHUR HILL CURTIS, LL.D., Professor of Natural Philosophy in the Queen's University\*.

IN no elementary treatise on Experimental Physics with which I am acquainted is any reference made to extraordinary *Reflection*; and I have known several instances where, from this omission, students have been led, though somewhat illogically, to the inference that in crystals producing double *Refraction* the ordinary law of *Reflection* is satisfied. On the other hand, in memoirs on molecular mechanics attention has frequently been drawn to the fact that the construction of Huyghens is as applicable to reflection as to refraction. Professor Haughton draws attention to this fact in his memoir on the equilibrium and motion of solid and fluid bodies (Trans. of the Royal Irish Academy, vol. xxi. part 2). Mr. Stoney has applied Huyghens's construction to the doubly reflected rays producing rings in striated calc-spar (Trans. R. I. A. vol. xxiv.); and Professor MacCullagh has, in the case of light, by the aid of his *theorem of the polar plane*, determined, on his theory, the intensities of the *two* reflected rays (Trans. R. I. A. vol. xviii. part 1). Still, in an experimental point of view, the existence of double reflection seems to be generally overlooked. If we suppose a wave-plane to traverse a crystal surrounded by any medium, whether ordinary or extraordinary, when this wave-plane reaches the extreme surface of the crystal it will give rise to *two reflected* rays, and to *one* or *two refracted* rays according as the surrounding medium is ordinary or extraordinary. To take the case most easily subjected to experiment, let us suppose a crystal surrounded by air, and a ray of light to fall upon it; part of this light is reflected, and part is refracted, the latter portion being in general divided into *two* rays, whether the crystal be uniaxial or biaxial; each of these rays will suffer double *reflection* at the point where it reaches the bounding surface of the crystal; and in the case where the two surfaces of contact of the crystal with the surrounding medium are *parallel* planes, or, more generally, when they intersect in a line parallel to the incident wave-plane, it is easy to see that the planes of polarization of the pair of reflected rays corresponding to any one of the two refracted rays produced at the first incidence, are the same as those corresponding to the other; for it is obvious that, when the above condition is fulfilled, the rays and wave-normals of one pair are parallel to those of the other; and whatever theory of light be adopted, the plane of polarization is known when the plane of the ray and wave-normal is determined. This is not only true of the two pairs of reflected rays *while within the crystal*, but, *for the same reason*,

\* Communicated by the Author.

continues true of the rays into which they may be divided subsequently by reflection and refraction at a common plane surface, and consequently is true, not only of the rays which reach the eye on emergence from the crystal, with which we are at present concerned, but also of the rays reflected back into the crystal at its *upper* surface.

The intensities of the four rays, however, are, as might be expected, in general different; and in fact, varying the position of the crystal, any one may be made to vanish while the other three continue to exist. The phenomena of crystalline reflection may be exhibited by the apparatus represented in the annexed figure.



It consists of a horizontal circular stage, B, movable round, and along, a vertical axis, C, passing through its centre. The crystal D (Iceland spar, well polished, for example) is placed on B. The light falls on it through a tube, A, covered with a cap, in which a small orifice is made. E is a tube situated similarly to A but at the opposite side of the crystal, while the height of the stage B is so adjusted that the light which passes through the tube A will, after reflection at the surface of the crystal which is in contact with B, and refraction at the opposite surface, pass through the tube E. The tubes A and E may be made movable round horizontal axes perpendicular to the plane of the figure, so as to allow of the angle of incidence being altered at will. The apparatus then being adjusted, if the eye be applied to the tube E, *five* images of the small orifice in the cap of the tube A will be seen—one formed by reflection at the *upper* surface of the crystal, which requires no consideration, and the other *four* by the double reflection of each of the refracted rays. As the stage is turned round its vertical axis these images may be *four*, *three*, or *two*—*four* in general, *three* when the azimuth of the crystal is such as to cause the intensity of one of the reflected rays to vanish, and *two* when the incidence and azimuth are such as to give but one

*refracted* wave-plane within the crystal, viz. when the plane of incidence contains the optic axis or axes, and the wave-normal corresponding to the two coincident refracted wave-planes coincides with an optic axis. If the cap of the tube A be replaced by a Nicol's prism with a small orifice, the images may be *four, three, two, or one* as the stage B is rotated (the last corresponding to the same arrangement as that which gives two images in the previous case) when in addition the Nicol's prism is so adjusted as to polarize the incident light in such an azimuth as to cause the intensity of one of the reflected vibrations to vanish. The planes of polarization of the several refracted rays may be determined by examining them by means of a Nicol's prism introduced into the tube E. If the tubes A and E be made of the same diameter, *one* Nicol's prism will be sufficient for all purposes.

Queen's College, Galway,  
April 1875.

**XLII. On Graphical Methods of solving certain simple Electrical Problems.** By Prof. G. CAREY FOSTER, F.R.S.\*

[With a Plate.]

**I**T is probably very seldom that the geometrical representation of the mathematical relations between physical quantities is as convenient, for purposes of investigation, as the corresponding analytical expression; but for purposes of exposition, as distinguished from those of investigation, geometrical constructions often possess considerable value. In particular, whenever they can be put into a simple form, their physical significance is more easily understood, than that of an algebraical formula, by those who are but little accustomed to mathematical modes of expression; and they generally exhibit with greater clearness the effect of a variation of any one of the related magnitudes. I have therefore thought that it might be worth while, for the sake of trying to draw increased attention to the utility of geometrical methods in elementary physical teaching, to point out in detail their application to a few important electrical problems, such as some of the simplest cases which come under Ohm's law of the relations between electromotive force, strength of current, and resistance.

If the equation which expresses Ohm's law be written in the three following ways—

$$\frac{E}{C} = R, \quad \frac{E}{R} = C, \quad C R = E,$$

\* Read before the Physical Society, November 7, 1874. Communicated by the Society.

where *E* stands for *electromotive force*, *C* for *strength of current*, and *R* for *resistance*, we have at once suggested three different modes of geometrical construction by means of rectangular coordinates, the coordinates representing in the three cases respectively (1) *electromotive force* and *strength of current*, (2) *electromotive force* and *resistance*, and (3) *strength of current* and *resistance*.

*I. Ordinates represent Electromotive Forces, and Abscissæ represent Strengths of Current.*

This system, according to which *resistance* comes to be represented by the *slope* of a straight line (that is, by the tangent of the angle which the line makes with the axis of *abscissæ*), was lately employed by M. Crova\* for the discussion of experiments relating to the degree of constancy possessed by so-called "constant" galvanic batteries; and its application to several other problems, including some of those treated by other methods in this paper, has been still more recently† pointed out by the same author. It is therefore not needful to discuss it further in this place.

*II. Ordinates represent Electromotive Forces, and Abscissæ represent Resistances.*

This system was used long ago by Ohm‡, and has been frequently employed since his time, though perhaps chiefly by practical electricians§. The following examples may serve to illustrate its application to questions connected with galvanic circuits in which there is a constant electromotive force.

Let *O A* (Plate VIII. fig. 1) represent the electromotive force of a battery, *O B* the resistance of the battery, and *BC* the resistance of the remainder of the circuit, this being made up of simple metallic conductors in which no additional electromotive force acts, then the slope of the straight line *AC*, or the *tangent* of the angle *AC O*, represents the strength of the current. It is obvious, by a glance at the figure, that the strongest current that the given battery could produce would be obtained by making the external resistance *BC* equal to nothing, and that it would be represented by the slope of the line *AB*, or by

\* *Comptes Rendus*, 6th April 1874, vol. lxxviii. p. 965.

† *Journal de Physique* (Sept. 1874), vol. iii. p. 278.

‡ *Die galvanische Kette mathematisch bearbeitet*, 1827.

§ See, for example, R. S. Culley, 'Handbook of Practical Telegraphy,' 1874, pp. 352-355; Latimer Clark, 'Elementary Treatise on Electrical Measurements,' 1868; G. K. Winter, "On Earth-Currents," *Journal of the Society of Telegraph-Engineers*, vol. ii. pp. 89-101; &c.

$\tan \angle ABO$ . Also it is evident that, if the external resistance is increased by equal amounts  $CC_1, C_1C_2, \dots$  each equal to  $BC$ , the strength of the current, as denoted by the slope of the line drawn from  $A$  to the points  $C, C_1, C_2, \dots$ , diminishes by smaller and smaller amounts for each equal increment of resistance, and that it would not vanish for any finite value of the resistance.

If any electromotive force acts in the part of the circuit external to the battery, its effect on the strength of the current can be represented by drawing through  $C$  a line  $CC'$  parallel to  $OA$ , and of length proportional to the external electromotive force, *upwards* if this electromotive force is *inverse*, *downwards* if it is *direct*,—and drawing the straight line  $AC'$  (fig. 2). If  $c$  be the point where this line cuts  $OC$ ,  $\tan \angle AcO$  measures the strength of the current. Of course the effect of any electromotive force outside the battery could also be represented by a diagram such as fig. 1, if the line  $OA$  were there taken to represent, not the electromotive force of the battery, but the total resultant electromotive force of the whole circuit.

If a line be drawn from  $B$  (fig. 1) parallel to  $OA$ , the length  $BD, BD_1, BD_2, \dots$  intercepted by the straight line through  $A$ , whose slope gives the strength of the current, represents the difference of potential between the terminals of the battery, or, in other words, the electromotive force which is effective in maintaining a current in the external conductor. The figure shows that this varies between a maximum ( $=OA$ , the total electromotive force of the battery) when the external resistance is infinite (contact broken) and a minimum ( $=0$ ) when the external resistance is nothing. If two values,  $BD$  and  $BD_1$ , of the externally effective electromotive force are known, which correspond respectively to two known values  $BC$  and  $BC_1$  of the external resistance, it is evident that the electromotive force and internal resistance of the battery will be given by drawing the straight lines  $CD$  and  $C_1D_1$ , producing them till they meet in  $A$ , and letting fall from  $A$  a perpendicular  $AO$  on  $CB$  produced:  $AO$  and  $OB$  then represent respectively the values required. Experimentally, the values to be given to  $BD$  and  $BD_1$  could be found by direct measurement with an electrometer; or they could be got from the relation  $e' = cr'$ , where  $e'$  is the externally effective electromotive force and  $c$  the current as measured by a galvanometer in a circuit of external resistance  $=r'$ .

From the above relations it is easy to deduce a construction, which may sometimes be of practical use, for finding the permanent resistance and electromotive force of a constant battery from two deflections of a galvanometer without using trigonometri-

*cal tables.* This construction requires to be slightly modified according to whether the instrument used is a tangent-galvanometer or a sine-galvanometer. It is as follows:—

1. *For a tangent-galvanometer.*—The battery is connected in simple circuit with a tangent-galvanometer, and the deflection  $\alpha$  of the galvanometer is observed; then a known resistance  $r'$  is added to the circuit and the deflection is observed again. Let the second deflection be denoted by  $\alpha'$ . The following construction then gives the electromotive force of the battery ( $=e$ ) and the permanent resistance of the circuit ( $=r$ ).

From any point A in the straight line O A (fig. 3) draw A P, making the angle O A P  $=\alpha$ ; produce O A to A', making A A' proportional to the added resistance  $r'$ , and from A' draw A' P', making the angle O A' P'  $=\alpha'$  and on the same side of O A as A P. Since  $\alpha'$  is less than  $\alpha$ , the straight lines A P and A' P' will intersect. From the point of intersection Q draw Q O perpendicular to O A. Then O A represents the permanent resistance of the circuit, and Q O represents the electromotive force, in terms of that electromotive force taken as unity which, if it acted in a circuit of unit resistance, would generate a current capable of causing a deflection of  $45^\circ$  on the particular galvanometer employed.

2. *For a sine-galvanometer.*—Let  $\beta$  be the deflection observed when there is no extra resistance, and  $\beta'$  the deflection when an additional resistance  $r'$  has been inserted in the circuit. Make B B' (fig. 4) proportional to  $r'$ , make the angles O B P and O B' P', on the same side of B B', equal respectively to  $\beta$  and  $\beta'$ , and let B P and B' P' intersect at the point Q. Draw Q O to bisect the external angle B Q P', and cutting B' B produced in O; then O B represents the permanent resistance of the circuit, while the radius of a circle drawn with the point O as centre so as to touch the straight lines B P and B' P' measures the electromotive force, the unit of measurement for the latter being the electromotive force which, in a circuit of unit resistance, would give a current strong enough to deflect the galvanometer used through  $90^\circ$ .\*

If the constructions indicated above are carried out for several different values of the external resistance, it is clear that, with a strictly constant battery, lines drawn according to the same rule

\* It may be worth while to point out that any galvanometer may be used as a sine-galvanometer, even though it is not provided with a graduation to show the angle through which it has been turned. It is only needful, after setting the instrument so that the zero of the scale is exactly below the needle while the current is passing, to interrupt the current; the needle then swings away from the zero-mark, returning to the magnetic meridian; and the angle now indicated by it is the angle through which the galvanometer has been turned from the meridian.

as  $AP$  and  $A'P'$ , in the case of a tangent-galvanometer, will all pass through the same point, and that, in the case of a sine-galvanometer, all lines drawn in the same way as  $BP$  and  $B'P'$  will be tangents to the same circle.

These constructions are so simple and can be so quickly made with sufficient accuracy, that by means of them the effect of altering the resistance of a circuit or the number or arrangement of the cells of a battery can be exhibited to a class by the help of actual measurements made during a lecture; but in order to make the process still more rapid, I have had an apparatus made, which may be called "A Galvanometric Slide-Rule," whereby, when two deflections of a galvanometer have been observed corresponding to a known difference of resistance, the permanent resistance and electromotive force of a battery can be ascertained in the course of a few seconds. The general arrangement of this apparatus is shown in fig. 5, which is drawn to a scale of about  $\frac{1}{20}$ .  $MN$  is a wooden base about 155 centims. long by 15.2 centims. wide, and 4.7 thick, with a groove in the upper surface, of the shape shown in fig. 5a, running from end to end. On the vertical side shown in the figure there is a scale 150 centims. long, divided into millimetres and numbered towards right and left from zero at a point  $A$  50 centims. from  $M$  and 100 centims. from  $N$ . Exactly above the zero mark of the scale is a small brass stud, the axis of which passes through the centre of a small graduated quadrant of 12 centims. radius. Another, similar quadrant,  $A'$ , with a brass stud at the centre is attached to a small board which slides on the upper side of  $MN$  and can be clamped by a screw in any position between  $A$  and  $N$ . There is also a vertical scale 65 centims. long, divided into millimetres and numbered from the bottom upwards, which is fastened to a sliding piece  $C$ , whereby it can be clamped in any position between  $M$  and  $A$ . The faces of the vertical scale and of the quadrants  $A$  and  $A'$  are flush with the face of the horizontal scale  $MN$ . Two thin silk cords, stretched by small weights, are passed over pulleys at  $P$  and  $P'$ , and attached one to each of the pins at the centres of the quadrants  $A$  and  $A'$ . The pulleys are so placed that the cords are very nearly in the same vertical plane as the scales  $MN$  and  $CQ$ . The apparatus is used as follows:—The pulley  $P$  is raised or lowered until the cord fixed at  $A$  shows, upon the corresponding quadrant, the deflection obtained on the tangent-galvanometer when no extra resistance is added to the circuit; the sliding piece carrying the quadrant  $A'$  is then moved towards right or left so that the number of centimetres in the distance  $AA'$  may be the same as the number of units of resistance (or, if more convenient, so that it may be a simple multiple or submultiple of this number)



added to the circuit in order to get a second reading of the galvanometer; then the pulley  $P'$  is adjusted so that the cord passing over it may indicate upon the quadrant B the galvanometer-deflection obtained after introducing the resistance corresponding to  $A A'$ ; and lastly the vertical scale is moved so that a vertical line drawn through the centre of the division-marks and continued downwards to meet the horizontal scale at O may be exactly behind the point Q, where the cords  $A P$  and  $A' P'$  cross each other. We have then only to read off the horizontal and vertical distances,  $A O$  and  $O Q$ , to get the permanent resistance and electromotive force of the circuit\*. To adapt the apparatus to use with a *sine-galvanometer*, it would be only necessary to replace the vertical scale  $O Q$  by a quadrant marked with concentric circular arcs, each differing from the next by 1 millim. in radius.

The following additional examples may be given of the same mode of treatment in connexion with allied problems:—

*Development of Heat in a Galvanic Circuit.*—Draw  $OC$  (fig. 6) horizontally to represent the resistance of the circuit, and  $OA$  vertically to represent the electromotive force; from  $A$  draw  $AC$  and also  $AD$  at right angles to  $AC$ ; then  $OD$  represents the heat produced in the circuit per unit of time. It is of course to be understood that  $OA$  denotes not necessarily the electromotive force of the battery, but the resultant electromotive force of the whole circuit—that is, the algebraic sum of all the electromotive forces which act anywhere in it. If  $OB$  denote the resistance of the battery and  $BC$  the remaining resistance of the circuit, and if  $BA'$  be drawn vertically,  $A'E F$  horizontally, and  $A'D'$  at right angles to  $AC$ ,  $E F$  will denote the heat generated in the battery, and  $B D'$  the heat generated in the external part of the circuit.

*Strength of Currents in the different branches of a divided Circuit.*—In considering this problem it is needful first of all to have a mode of representing geometrically the combined resistance of two or more conductors connected in “multiple arc.” Let  $AB$  and  $BC$  in the same straight line (fig. 7) represent the resistances of two conductors taken separately. Draw  $AB'$  equal to  $AB$  and at right angles to it; join  $B'C$ , and through  $B$  draw a line parallel to  $AB'$  and cutting  $B'C$  in  $L$ ; then  $BL$  represents the combined resistance of the two conductors. The same process is applicable to any number of conductors. Thus, let  $AB$ ,  $BC$ , and  $CD$  (fig. 8) represent the separate resistances of three conductors connected in multiple arc. Making the con-

\* The quadrant A is made so that it can be turned aside to allow of the vertical scale being brought close up to the zero-point of the horizontal scale when low battery-resistances have to be measured.

struction indicated above,  $BL$  represents the resistance equivalent to  $AB$  and  $BC$  in multiple arc. Draw  $LM'$  parallel to  $ABCD$ , make  $CM = BL$ , draw  $MM'$  at right angles to  $BC$ , join  $M'D$ , and draw  $CN$  perpendicular to  $CD$ .  $CN$  then represents the joint resistance of the three conductors.

Now consider a conducting-system such as that indicated in fig. 9, where two points,  $P$  and  $Q$ , are connected through three conductors whose resistances are respectively  $r$ ,  $r_1$ , and  $r_2$ ; and let a battery of electromotive force  $e$  make part of the first conductor. The strength of the currents and the distribution of potential in the various parts of the system can be represented as follows:—Take  $OA$  (fig. 10) to represent  $r$ , from  $O$  draw  $OB$  and  $OC$  in opposite directions perpendicular to  $OA$ , make  $CC'$  equal to  $OC$  and perpendicular to it, draw  $BC'$  cutting  $AO$  produced in  $D$ ; then  $OD$  represents the joint resistance of  $r_1$  and  $r_2$ . Draw  $AE$  perpendicular to  $AO$  to represent the electromotive force  $e$ , and join  $ED$ . Then  $\tan \angle ADE$  represents the strength of the current in the battery and the sum of the currents in the two parallel branches. These may be obtained separately thus: let the point of intersection of  $ED$  and  $OB$  be denoted by  $F$ ; then  $OF$  represents the difference of potential between the points  $P$  and  $Q$  or the electromotive force which is effective in the two conductors of resistance  $r_1$  and  $r_2$ . In  $OA$  make  $OF' = OF$  and draw  $F'B$  and  $F'C$ ; we have then, for the strength of the currents in the conductors whose resistances are represented by  $OB$  and  $OC$ ,  $\tan \angle OBF'$  and  $\tan \angle OCF'$  respectively.

Next let *two* of the conductors connected together at  $P$  and  $Q$  contain galvanic batteries, and, as before, let the resistance of the branch containing one battery be  $r$ , while that of the branch containing the other is  $r_1$ , and let the electromotive forces be  $e$  and  $e_1$  respectively. If the batteries are so connected that both tend to make the potential at  $P$  differ from that at  $Q$  in the same sense, we have an arrangement of which a special case is presented by Poggendorff's "compensation method" for the comparison of electromotive forces. To obtain a geometrical expression for the strengths of the currents in the various parts of the circuit in the general case (that is, without assuming that there is "compensation" in any branch), we may proceed in the following manner:—Take  $OA$  and  $OB$  in the same straight line (fig. 11) to represent the resistances  $r$  and  $r_1$  of the two branches including the batteries, and  $OC$  at right angles to  $AB$  to represent the resistance  $r_2$  of the third branch. In  $CO$  produced make  $OA_1 = OA$ , and  $OB_1 = OB$ , also draw  $A_1A_2$  equal and parallel to  $OA$  and  $B_1B_2$  equal and parallel to  $OB$ , and join  $A_2C$  and  $B_2C$ . Let  $A_2C$  cut  $OA$  in  $N$ , and let  $B_2C$

cut  $O B$  in  $M$ . From  $A$  draw  $A E$  at right angles to  $A O$  to represent the electromotive force  $e$ , and draw  $E M$  cutting  $O C$  in  $E'$ ; similarly, from  $B$  draw  $B F^*$  to represent the electromotive force  $e_1$ , and draw  $F N$  cutting  $C O$  (produced) in  $F'$ . Then  $F' E' = F' O + O E'$  represents the electromotive force which is effective in the conductor of resistance  $r_2$  represented by  $O C$ , and  $A E - F' E'$  and  $F B - F' E'$  represent the electromotive forces which are effective in the branches of resistance  $r$  and  $r_1$  respectively.

### III. Ordinates represent Strength of Current, and Abscissæ represent Resistances.

With this system of coordinates, electromotive force is expressed by the area of a rectangle. Thus, if a given battery produces a current whose strength is represented by the ordinate  $M m$  of the point  $M$  (fig. 12), in a circuit the resistance of which is represented by the abscissa  $O m$  of the same point, its electromotive force must be proportional to the area of the rectangle  $O M$ ; and if the battery is "constant," the currents, represented by the ordinates  $M_1 m_1$ ,  $M_2 m_2$ , and corresponding to the resistances denoted by the abscissæ  $O m_1$ ,  $O m_2$ , will be such that the areas of the rectangles  $O M$ ,  $O M_1$ , and  $O M_2$  are all equal; and hence the characteristic property of the battery will be expressed by the curve which is the locus of the points  $M$ ,  $M_1$ , &c.—that is to say, by a rectangular hyperbola whose asymptotes are the axes of no current and no resistance. When the hyperbola characteristic of a given battery is drawn, it is of course easy by measuring coordinates to find what current would flow through a given resistance, or conversely to find what must be the resistance of the circuit in order that the current may have a given strength; but the difficulty of tracing an hyperbola with accuracy greatly lessens the practical utility of this method of calculation. Since, however, the asymptotes are fixed, each hyperbola is completely defined when one point of it is given; and, in like manner, when the corresponding values of current and resistance are known in any one case for a given battery, each is determined for any other case when the value of the other is given. Accordingly the actual drawing of an hyperbola is not necessary; for when one point is assigned, any other points corresponding to given problems can be easily found.

For instance, let the coordinates of the point  $M$  (fig. 13), referred to the axes  $O X$  and  $O Y$ , represent respectively the

\*  $B F$  must be drawn in the *opposite* direction to  $A E$  if, as supposed above, the batteries are so connected that the difference of potential between the points  $P$  and  $Q$  due to each battery separately is of the *same* sign.

resistance of a conductor and the strength of the current produced in it by a given electromotive force, and let it be required to find the strength of the currents which the same electromotive force would generate in conductors whose resistances are respectively represented by the abscissæ  $O m_1$  and  $O m_2$ . Through  $M$  draw a line  $M P Q$  parallel to  $O X$ , and through  $m_1$  and  $m_2$  draw  $m_1 P$  and  $m_2 Q$  parallel to  $O Y$ ; join  $O P$  and  $O Q$ , and let  $p$  and  $q$  be the points in which  $O P$  and  $O Q$  respectively cut  $M m$ ; then  $m p$  and  $m q$  will represent the strengths of the required currents; and if lines be drawn parallel to  $O X$  through  $p$  so as to intersect  $m_1 P$  in  $M_1$ , and through  $q$  so as to intersect  $m_2 Q$  in  $M_2$ ,  $M_1$  and  $M_2$  will be points whose coordinates, like those of  $M$ , represent corresponding values of resistance and strength of current. The points  $M, M_1$ , and  $M_2$ , therefore, lie upon the same rectangular hyperbola.

In a similar way we may treat many problems of the same sort as those discussed above by aid of what for distinction may be called Ohm's construction; but as the constructions, arising from the choice of resistance and strength of current as coordinates are usually rather more complex than those previously given, and as I have not come across any cases in which they appear to be decidedly more expressive, I will only give two additional examples.

*To find the permanent resistance and the electromotive force of a battery from observations of the strengths of two currents corresponding to resistances which differ by a known amount.*—Let  $m M$  (fig. 14) represent the strength of the current when the resistance of the circuit has an unknown value represented by the (unknown) abscissa  $O m$ ; and let  $n N$  express the strength of the current when the resistance has been increased by a known amount denoted by  $m n$ . Through  $M$  and  $N$  draw straight lines parallel to  $m n$ , and let  $N_1$  and  $M_1$  be the points where these lines respectively intersect  $n N$  (produced) and  $m M$ . Draw the straight line  $N_1 M_1$  and produce it to intersect  $n m$  produced in  $O$ ; then  $O m$  represents the original resistance of the circuit, and the rectangle on the base  $O m$  with altitude  $m M$ , or the rectangle on the base  $O n$  with altitude  $n N$ , represents the electromotive force.

*The heat produced in unit of time by a constant current of given strength traversing a conductor of given resistance* can be represented by the volume of a right square prism, two of whose dimensions represent the strength of the current, while the third represents the resistance; and in the case of a battery of constant electromotive force, the relation between the resistance of the circuit and the heat produced in unit of time can be expressed generally as follows:—Take three rectangular axes,  $O X, O Y,$

and O Z (fig. 15); in O X take O K to represent the resistance, and in O Y take O M so that the area of the rectangle K M represents the electromotive force, and therefore O M the strength of the current. Similarly, take O N in O Z also to represent the strength of the current. Then the heat generated in unit of time is proportional to the contents of the rectangular parallelopiped O P, constructed upon the lines O K, O M, and O N. The locus of P is the intersection of two equal and similar hyperbolic cylinders, whose equations are respectively  $xy = \text{constant} = \text{electromotive force}$ , and  $xz = \text{constant} = \text{electromotive force}$ , and is itself a rectangular hyperbola in the plane of O X and O Q, and having these lines for asymptotes. If O K' represent the internal resistance of a battery, and K' K the external resistance, the heat generated inside the battery is represented by the parallelopiped O P', and that generated in the external conductor by the parallelopiped K' P.

XLIII. *Remarks on Helmholtz's Memoir on the Conservation of Force.* By ROBERT MOON, M.A., Honorary Fellow of Queen's College, Cambridge\*.

THE following observations are offered on the assumption that Helmholtz's memoir "*Ueber die Erhaltung der Kraft*" (Berlin, bei G. Reimer, 1847), the original of which I have not had an opportunity of examining, is correctly represented by Professor Tyndall's translation contained in Taylor's *Scientific Memoirs* for 1853.

I pass by for the present the introductory matter and the disquisition on the conservation of *vis viva* contained in the memoir; nor shall I now discuss the grounds upon which the author rests his primary induction that the constancy of "the sum of the tensions and *vires vivæ*" (which undoubtedly holds "in all cases of the motion of free material points under the influence of their attractive and repulsive forces, whose intensity depends solely on the distance") represents a general law of nature.

I come to the author's "special application" of the principle, or to what would be more correctly designated as his attempts to demonstrate its truth in cases of motion where we do *not* deal with "material particles under the influence of their attractive and repulsive forces," but with continuous masses the different portions of which act upon each other otherwise than by attraction or repulsion; and of these cases of motion I shall confine myself to one, viz. where "a medium . . . is traversed by a train of waves"—a case in which Dr. Helmholtz evidently considers

\* Communicated by the Author.

that "the principle of the conservation of *vis viva*" holds. (Taylor's *Scient. Mem.* 1853, p. 127.)

Now in order to establish the truth of the conservation of force as that principle is propounded by Dr. Helmholtz—in other words, in order to show that the constancy of "the sum of the tensions and *vires vivæ*" holds in the above or any other instance, it is obviously necessary that we should derive by independent methods values for the *vis viva* and "the sum of the tensions"—equivalent to the kinetic and potential energies of a more modern nomenclature,—and that we should then show that the sum of the expressions so arising is always constant.

As Dr. Helmholtz, while attempting to prove that the conservation of force holds in the case of a train of waves traversing a medium, confines all his efforts to establishing the constancy of the *vis viva*, taking not the smallest notice of "the sum of the tensions," I am led to conclude that he regards the latter as always vanishing in cases of motion of the kind in question. It is to be regretted that so important a step should have been passed over in silence\*. In the mean time I assume that the author relies on the principle—which I have seen and heard enunciated—that the mutual normal actions between elements in contact may be neglected in forming the equation of *vis viva*.

The method of estimating the *vis viva* adopted by Dr. Helmholtz in the case we are considering, I believe to be utterly erroneous and misleading. At present, however, I do not desire to dwell upon this point, but shall proceed to show, as I hope to do strictly:—

I. That if it were true that when waves traverse a medium the sum of the tensions disappears from, or is constant in, the equation of *vis viva*, that fact would be fatal to the theory of the conservation of force proposed by Dr. Helmholtz.

II. That it is *not* true that the sum of the tensions in general vanishes under the circumstances supposed.

III. That the principle of *vis viva*, and therefore the principle of the conservation of force as propounded by Dr. Helmholtz, does *not* hold in the case of waves traversing a medium.

I. It is well known that a wave in which the vibration is normal to the front may be propagated in a cylindrical tube filled with air in a direction parallel to the axis, without undergoing any change in its length, or in the mode in which the condensation and particle-velocity are distributed throughout it,

\* Clausius makes upon Helmholtz's memoir the following remark:—"It is to be regretted that the author of this ingenious essay has not entered more fully into the details of his subject. From this cause certain portions appear to me to be incorrect."—Taylor's *Scientific Memoirs*, Nov. 1852, p. 6, note.

provided that we neglect the friction of the sides of the tube upon the air within it.

This will be the case whatever be the form of disturbance, provided only

1. That the velocities and condensations are small, and follow the law of continuity,
2. That the condensation at any point bears a fixed ratio to the particle-velocity at that point (*Encyc. Met. Art. Sound, No. 128*).

Suppose that we have a wave consisting of condensation only which fulfils these conditions; and suppose for simplicity, though this is by no means essential, that the condensation is distributed symmetrically about the middle point of the wave, and that it has a single maximum, which will, of course, be that of the middle point. The particle-velocity throughout will be in the same direction—that, namely, of transmission.

Suppose, further, that we have in a different part of the tube a second condensed wave, equal in length to the former, having also but one maximum, viz. at its middle point, where the condensation is equal to the condensation at the middle point of the first wave, and having at equal distances from the middle point on either side of it the same amount of condensation as the first wave at the same distance from its middle point.

I shall also suppose that at equal distances from their respective middle points the particle-velocity in each wave is the same in amount but *opposite in direction*. It follows that the waves will move in opposite directions.

Consider the waves, first, as they advance towards each other; next, as after the meeting they overlap; finally, at the period of complete occultation, when the middle point of the one wave coincides with the middle point of the other.

Before meeting, the *vis viva* of either wave will be constant, and the *vis viva* of the system of two waves will be double that of either taken singly.

When the waves overlap, the condensation at any point of the overlapping portions will be the sum of the condensations of the portions superposed, but the particle-velocity at this point will be the *difference* of the velocities of the superposed portions taken singly. In this part of the system, therefore, *i. e.* in each element of the overlapping portion of the waves, *vis viva* will be lost; so that, as the waves after meeting will gradually more and more overlap, the *vis viva* of the system will continually diminish, till, when the position of complete occultation is arrived at, the velocity at each point, and consequently the *vis viva* of the system, will have wholly vanished.

As the waves emerge from occultation, velocity and conse-

quently *vis viva* will constantly be generated, till, as the waves become extricated the one from the other, the *vis viva* will be, what it will ever after remain, exactly what it was at first.

Hence, if it were true, as Dr. Helmholtz assumes, that the normal actions disappear from the equation of *vis viva* when we consider the internal motions of continuous masses, that fact alone would suffice to demonstrate the entire failure of his principle of the conservation of force in cases of motion such as that we have been considering.

II. That the sum of the tensions does not in general vanish when a wave traverses a medium may be seen as follows:—

Let  $x$  and  $y$  be the ordinates (measured parallel to the axis of the tube) in the state of rest and at the time  $t$  of one surface of an element made by planes perpendicular to the axis,  $p$  the pressure at the same surface,  $D$  the density of equilibrium. The equation of motion may be put under the form

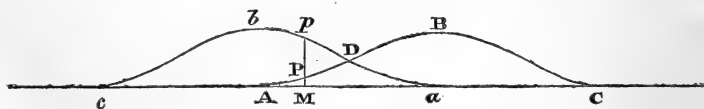
$$0 = D \frac{d^2 y}{dt^2} dx + \frac{dp}{dx} dx;$$

whence, multiplying by  $\frac{dy}{dt} dt$  and integrating, we get for the equation of *vis viva* the following, viz. :—

$$0 = \frac{D}{2} \int dx \left( \frac{dy}{dt} \right)^2 + \int dt \int dx \frac{dy}{dt} \frac{dp}{dx},$$

the integration being effected between any limits we may fix upon.

Suppose that we have two waves of condensation, such as those already described, travelling in opposite directions; and ( $x$  and  $y$  being measured parallel to  $cAC$  in the annexed figure) let the ordinate perpendicular to  $cAC$  of the curve  $ABC$  represent the condensation in the wave which moves towards the right, in which direction we will suppose  $x$  and  $y$  measured positively; while the corresponding ordinate of the curve  $abc$  represents the condensation in the wave which moves to the left.



Assuming the truth of Boyle's law in cases of motion (which it will suffice to do for the purposes of this paper), if the wave corresponding to  $ABC$  (or, as for brevity I shall designate it the wave  $ABC$ ) stood alone, we should have  $\frac{dp}{dx}$  positive through-



out the hinder (left hand) half of the wave, and negative throughout the front half; and as the velocity in A B C is throughout positive, it follows that throughout the hinder half of A B C we shall have  $\frac{dp}{dx} \frac{dy}{dt}$  positive, while throughout the front half of A B C

the same function will be negative. For the entire wave, therefore, it is clear, from the symmetrical form of vibration which we have ascribed to it, that the sum of the tension will be zero\*.

If we now consider the wave *a b c* taken singly, we shall have throughout its hinder (*right* hand) half  $\frac{dp}{dx}$  negative, while throughout its front half  $\frac{dp}{dx}$  will be positive; and the velocity throughout *a b c* being negative, we shall have  $\frac{dp}{dx} \frac{dy}{dt}$  positive throughout the hinder half of the wave, and negative throughout the front half.

Thus, in the case of either wave taken separately, the positive and negative parts of the term in the equation of *vis viva* depending on the tensions will counterbalance each other, and the tensions will wholly disappear from that equation. But when the waves are superposed, or interfere, as, for instance, in the manner represented in the figure, this mutual balance of the opposing terms will cease to exist, as I shall now proceed to show.

The figure is supposed to represent the state of things occurring *after* the period of complete occultation, when the front half of each wave has entirely emerged, and while the hinder halves have in part emerged, but as to the remainder are still in the state of superposition.

Draw *p P M* perpendicular to *c A C*, and on the left of *D*, the point of intersection of the curves A B C, *a b c*.

When the waves are separate and non-interferent, a stratum of the hinder half of either wave of the undisturbed breadth *dx*, in the case of the one corresponding to *P M*, in the other to *p m*, would give rise to a positive term in the equation of *vis viva*.

But when these elementary portions of the two waves become superposed, although the condensation of the combination will be the sum of the condensations of the two elements taken separately, yet, inasmuch as the values of  $\frac{dp}{dx}$  for the separate elements

have opposite signs, the sign of  $\frac{dp}{dx}$  for the combination may be

\* Though less obvious, the same is equally true whatever be the form of vibration, provided that the wave is such as to be transmitted without undergoing change in its length, or form of vibration.

positive or negative according to circumstances. If the sign of  $\frac{dp}{dx}$  in the combination be positive, since it will be multiplied in the equation of *vis viva* by a negative velocity (for the velocity in the combination will be the *difference* of the velocities of the components, and the velocity in *abc* is here predominant), we shall have at this point  $\frac{dp}{dx} \frac{dy}{dt}$  negative; so that this portion of the wave, instead of aiding to balance the negative tensions prevailing throughout the front halves of the two waves, as its components would have done if the two waves had continued separate, will, so to speak, go over to the side of the latter.

On the other hand, if at this point of the combined disturbance  $\frac{dp}{dx}$  be negative, its value will be less in amount, irrespective of sign, than what it would have been for the wave *abc* taken separately, at the same time that, as before, it will be multiplied by a negative velocity, but a velocity which will be less than the velocity with which  $\frac{dp}{dx}$  would be multiplied if we were dealing with the wave *abc* separately. Hence, though at this point the element of the combined disturbance would, as in the case of each of its components taken separately, tend to counteract the negative tensions of the emerged front halves of the two waves, yet it would do this in a less degree than one only of those components would do when taken separately (the wave *abc* to wit), and therefore, *à fortiori*, in a less degree than both.

If we had drawn *p P M* on the right side of *D*, we should have arrived at precisely the same conclusion, though in a slightly different manner. It thus appears that, while the negative tensions at the time represented in the figure are precisely the same as when the waves were separate, the positive portion of the tensions will be diminished in amount, so that they will no longer counterbalance the former. On the whole, therefore, the sum of the tensions, instead of being zero, will give rise to a negative term of finite magnitude in the equation of *vis viva*.

III. If it should be supposed that the fact of the sum of the tensions not vanishing in the equation of *vis viva* may afford a possible source of compensation for the loss of *vis viva* which it has been shown may arise from the interference of waves, the foregoing investigation will suffice to show the fallacy of this view. For, in the case of motion above considered it is evident that the destruction of the *vis viva* may be accompanied by the development of a *negative* term due to the tensions; in which case there will be a loss of energy, not only through the destruc-

tion of *vis viva*, but by reason of the fact that what *vis viva* is left will be more or less counteracted by the presence of the negative term due to the tensions.

It is clear, therefore, that the conservation of *vis viva* cannot be relied on as holding in cases of the intersection of waves traversing continuous masses, and that what Dr. Helmholtz has offered to our attention as a universal law of nature is completely contradicted by fact in cases such as those we have been considering.

If we advert to the original derivation of the equation of *vis viva* from the principle of virtual velocities, if we reflect how completely the arbitrary displacement of the *points of application* of the respective forces forms the characteristic feature of the principle of virtual velocities, and bear in mind that the transition from that principle to the equation of *vis viva* is effected simply by the substitution of the actual for the arbitrary motions—if we keep in view these various considerations, it can hardly be matter of surprise that, in treating of the internal motions of continuous masses it should have come to be considered that the only terms depending on the internal actions which need be taken into account in forming the equation of *vis viva* consist of pairs of equal and opposite forces multiplied by a common displacement or common velocity (that, namely, of the common point of application of the forces), and consequently that no such terms will appear in that equation.

That this mode of considering the subject, however specious, must be entirely erroneous, sufficiently appears, if I mistake not, from what has preceded; but it is of the highest importance that the *mode* as well as the *fact* of the fallacy should be clearly apprehended; and to this part of the subject I propose now to address myself.

Let  $p_1, p_2$  be the pressures, and  $v_1, v_2$  the particle-velocities at the time  $t$  at the surfaces the ordinates of whose positions of rest are respectively  $x+dx$  and  $x+2dx$ ;  $p_{-1}, p_{-2}, v_{-1}, v_{-2}$  the corresponding quantities for the surfaces as to which  $x-dx$  and  $x-2dx$  are the ordinates of the positions of rest.

The equation of motion of the first element may be put under the form

$$0 = D \frac{dv}{dt} dx + p_1 - p;$$

multiplying which by  $v dt$  we get

$$0 = D v \frac{dv}{dt} dt dx + p_1 v dt - p v dt.$$

The corresponding equations for the elements in contact with

the first will be

$$0 = Dv_1 \frac{dv_1}{dt} dt dx + p_2 v_1 dt - p_1 v_1 dt,$$

$$0 = Dv_{-1} \frac{dv_{-1}}{dt} dt dx + p v_{-1} dt - p_{-1} v_{-1} dt.$$

Hence, corresponding to the different elements of the entire wave, we shall have a series of equations, such as

$$0 = \&c.,$$

$$0 = Dv_{-2} \frac{dv_{-2}}{dt} dt dx + p_{-1} v_{-2} dt - p_{-2} v_{-2} dt,$$

$$0 = Dv_{-1} \frac{dv_{-1}}{dt} dt dx + p v_{-1} dt - p_{-1} v_{-1} dt,$$

$$0 = Dv \frac{dv}{dt} dt dx + p_1 v dt - p v dt,$$

$$0 = Dv_1 \frac{dv_1}{dt} dt dx + p_2 v_1 dt - p v_1 dt,$$

$$0 = Dv_2 \frac{dv_2}{dt} dt dx + p_3 v_2 dt - p_2 v_2 dt,$$

$$\&c. = \&c.$$

Taking the sum of these, observing that the first and last terms will vanish, the particle-velocity at the extremities being either zero or infinitely small, we get

$$\begin{aligned} 0 &= \Sigma \left( Dv \frac{dv}{dt} dt dx \right) + \Sigma p (v_{-1} - v) dt \\ &= \Sigma \left( Dv \frac{dv}{dt} dt dx \right) + \Sigma p \left( v - \frac{dv}{dx} dx - v \right) dt \\ &= \Sigma \left( Dv \frac{dv}{dt} dt dx \right) - \Sigma p \frac{dv}{dx} dx dt \\ &= \int_x Dv \frac{dv}{dt} dt - \int_x p \frac{dv}{dx} dt, \end{aligned}$$

the integration being extended over the entire wave, or

$$0 = \int_x Dv \frac{dv}{dt} dt + \int_x v \frac{dp}{dx} dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

(since  $\int_x p \frac{dv}{dx} = pv - \int_x v \frac{dp}{dx}$ , the first term on the right-hand side of which equation vanishes when the integration is extended over the entire wave, the velocity vanishing at the extremities of the wave).

Integrating ( $\alpha$ ) with respect to  $t$ , we get, as before, the equation of *vis viva*; this mode of deriving which enables us to see the error committed in supposing that, when the equation is formed for a continuous mass, the equal and opposite forces acting at the common boundary of two elements will be multiplied by the same velocity, viz. that of the bounding surface.

It is clear that we must treat the motion of each element exactly as if it were collected at its centre of gravity—that the velocities by which we multiply the forces acting upon it are not the velocities of their actual points of application, but that of their hypothetical point of application, viz. the centre of gravity of the element—in other words, that the velocity by which we multiply must be the average velocity prevailing throughout the element; from which it follows that the force  $p$ , for example, when regarded as acting on the element originally considered, must be multiplied by the velocity  $v$ ; but when it is regarded as acting on the element immediately in the rear of the former, it must be multiplied by  $v_{-1}$  or  $v - \frac{dv}{dx} dx$ ; so that, instead of those equal and opposite forces disappearing from the equation of *vis viva*, they will give rise to a residuum, viz.  $p \frac{dv}{dx} dx$ ; and the sum of these small terms taken for the entire wave will in general be a finite quantity.

It can hardly be necessary that I should point out the bearing which the foregoing conclusions have upon the applicability, when compressible bodies are dealt with, of the principle of virtual velocities.

6 New Square, Lincoln's Inn,  
March 3, 1875.

XLIV. *On the Flow of Electricity in a uniform plane conducting Surface.*—Part I. By G. CAREY FOSTER, F.R.S., and OLIVER J. LODGE\*.

[With a Plate.]

1. **T**HE objects of the following paper are:—first, to show that the most important laws relating to the flow of electricity in a plane conducting sheet of uniform conductivity can be established by mathematical considerations of such a simple kind that there is no reason why they should not be introduced into ordinary teaching, as well as into the more complete elementary text-books of electricity; and in the second place, to describe methods that may conveniently be employed for testing

\* Read before the Physical Society, February 27, 1875. Communicated by the Society.

experimentally the theoretical conclusions, together with some results obtained by these methods.

The general subject treated of in this paper has attracted the attention of a considerable number of mathematicians and physicists. The earliest published investigation relating to it was contained in a remarkable memoir by Kirchhoff, which appeared in Poggendorff's *Annalen* in 1845 (vol. lxiv. p. 497). In this paper Kirchhoff established the general mathematical theory of the flow of electricity in an unlimited uniformly conducting-sheet, and in a limited sheet with a circular boundary, with so much completeness as to leave little for others to do beyond working out the application to special cases of the general principles he laid down, or finding other methods of establishing the conclusions he deduced from them.

We cannot better indicate the general plan of Kirchhoff's investigation than by quoting the following account of it from a paper by Professor W. Robertson Smith\*, to which we shall have to make further reference immediately:—"By an application of Ohm's law, he [Kirchhoff] expressed analytically the condition to be satisfied by  $v$  [the potential]. When the electricity enters and issues by a number of individual points, he found (apparently by trial) that an integral of the form  $\Sigma(\alpha \log r)$ , where  $r_1, r_2, \&c.$  are the distances of the point  $(x, y)$  from the successive points of entrance and issue, satisfied the conditions when the plate is infinite. For a finite plate, it is necessary that the boundary of the plate should be orthogonal to the curves

$$\Sigma(\alpha \log r) = \text{const.} \quad . \quad . \quad (3)$$

He was thus led to form the orthogonal curves whose equation he gives in the form

$$\Sigma(\alpha [r, R]) = \text{const.}, \quad . \quad . \quad (4)$$

where  $[r, R]$  is the angle between  $r$  and a fixed line  $R$ . These equations he applies to the case of a circular plate, completely determining the curves when there is one exit and one entrance point in the circumference, and showing that in any case a proper number of subsidiary points would make the equipotential lines determined by (3) cut the circumference at right angles. Kirchhoff's paper is throughout properly busied with the function  $v$ , and the stream-lines are only dealt with incidentally. There is no attempt to give a physical meaning to the equation (4)." To this we have only to add that Kirchhoff proved the accuracy of his theoretical deductions by determining experimentally the form and distribution of the equipotential lines on a circular disk with two electrodes on the edge, as well as (Pogg. *Ann.*

\* Proc. Edinb. Roy. Soc. 1869-70, pp. 79-99.

vol. lxvii. p. 344, 1846) the strength of the current at various parts of the disk; and that, from the expression for the difference of potential between the electrodes, he deduced by Ohm's law the resistance of a circular disk with two small electrodes anywhere upon it. In order to test experimentally the value thus obtained, he seems to have devised independently the arrangement now commonly known as Wheatstone's bridge; but, owing to the smallness of the resistance to be measured, he was unable to obtain satisfactory results.

Soon after the publication of Kirchhoff's paper, Smaasen\* gave an investigation of the flow of electricity in a plane conducting sheet, in which he takes account, in determining the potential, of the electricity given off to the air, and deduces the resistance of an infinite sheet with two small circular electrodes by a process which, though longer than that employed by Kirchhoff, may be regarded as more direct. It consists in finding the resistance of the space between two lines of flow at an infinitely small distance apart, and then extending by integration the expression thus obtained so as to make it apply to the unlimited sheet. In a subsequent paper† Smaasen determined by an analogous process the resistance of a conducting sphere, or of an unlimited conductor of three dimensions‡. Smaasen's treatment of the subject is, like Kirchhoff's, based chiefly upon the mode of distribution of the potential; the only investigation we are acquainted with which deals specially with lines of flow is contained in the paper by Professor W. Robertson Smith from which we have already quoted. The starting-point adopted by Professor Smith is the same as that from which we have set out in the following communication; and, indeed, we found, after making some progress in our own work, that several of our demonstrations (which we at first thought were new) had been already given by him, while all the chief conclusions were, as we have said above, implicitly contained in Kirchhoff's original memoir. Consequently, although the present paper contains a few minor results which, so far as we know, have not been pointed out explicitly before, we do not claim for its contents any essential novelty; and our only reason for venturing to publish it is that

\* Pogg. *Ann.* vol. lxi. p. 161.

† Pogg. *Ann.* vol. lxxii. p. 435.

‡ About the same time, the same subject was taken up by Ridolfi of Florence (*Il Cimento*, An. V. 1847, May-June), whose paper, however, we only know from the references of Beetz (in Dove's *Repertorium*, vol. viii. p. 147) and Poggendorff (Pogg. *Ann.* vol. lxxii. p. 449). No reference to this paper is given either in the Royal Society's Catalogue of Scientific Papers, or in the carefully compiled "Bibliographie" of the mathematical theory of the voltaic pile in Verdet's *Conférences de Physique* (*Œuvres de Verdet*, vol. iv. p. 351).

the mode of treatment adopted in it has enabled us to establish by strictly elementary mathematical methods, and so to render accessible to a greater number of readers, many of the conclusions which previous writers had arrived at by more abstruse processes.

2. In order to avoid ambiguity, it may be well to begin by giving a few general explanations and definitions of terms that will be frequently used in what follows. It will be assumed that, in all cases considered, the flow of electricity has attained a *stationary* condition—that is to say, that on the whole there is neither gain nor loss of electricity at any part of the sheet, but that at every instant the quantity that enters any part and the quantity that leaves it are equal. Positive electrodes, or such as supply positive electricity to the sheet, will be spoken of as “sources,” while negative electrodes will be termed “sinks.” The rate at which a source or a sink supplies or removes electricity will be spoken of as the “strength” of the source or sink.

Through every point of the sheet a straight line can be drawn such that no electricity crosses it at that point; the direction of a line so drawn through a given point is the “direction of the current” at that point. A “line of flow” or “stream-line” is a line drawn so that no electricity crosses it anywhere; or, in other words, it is a line whose direction at all points coincides with the direction of the current. The quantity of electricity flowing between two consecutive lines of flow is everywhere the same; for since no electricity crosses either of them, whatever quantity starts between them must remain between them throughout their whole course. It may be useful to observe that flow-lines are not loci of constant strength of flow, they are lines of direction simply.

The “strength of the current” at any point is given by the quantity of electricity which crosses, in unit time, a short line normal to the flow-line through the point, divided by the length of the line.

If a line be drawn so as to intersect the lines of flow everywhere at right angles, there will be no flow of electricity along it; but since the sheet on which the line is drawn is a conductor, this implies that all points of the line are at the same potential, or that the line is an “equipotential line.”

3. It is obvious that a line of flow and an equipotential line might be drawn through every point of a conducting sheet traversed by a current, so that, if it were possible to draw them all, the sheet would be completely covered by two sets of lines cutting each other at right angles. The general distribution, however, of the lines of each set can be correctly shown without drawing more than a limited number, if those that are drawn



are selected according to a definite and easily recognizable rule. For this purpose the most convenient rule to adopt in relation to the lines of flow, is to place them so that the total flow of electricity between each pair of consecutive lines is the same—and with regard to the equipotential lines, to place them so that the change of potential in passing from any one to the next consecutive line is the same. In the sequel, whenever a *system* of lines of flow, or of equipotential lines, is referred to, it is to be understood that the lines are placed so as to fulfil the above conditions.

*One Pole in an Infinite Sheet.*

4. In this case it is evident that the lines of flow are straight lines radiating out from the pole, and that the spaces between each pair of consecutive lines will convey equal currents if each line makes the same angle with the next. If a circle of radius  $r$  be drawn about the pole as centre, the quantity of electricity which crosses the whole circumference in unit of time, will evidently be the same whatever the value of  $r$ , and will be equal to the quantity  $Q$  supplied in the same time by the source. Hence, at distance  $r$  from the source, the strength of the current will be

$$\frac{Q}{2\pi r},$$

or inversely proportional to the distance  $r$ .

It is evident also, either from general considerations of symmetry, or from the condition that equipotential lines and lines of flow must intersect each other at right angles, that the equipotential curves for the case we are considering are circles having the source at their common centre.

5. If  $R$  be the resistance to the radial flow of electricity across the annular portion of the sheet bounded by circles at the potentials  $V_1$  and  $V_2$ , we have, by Ohm's law,

$$V_1 - V_2 = QR;$$

whence, since  $Q$  is constant, equal differences of potential will be found at the boundaries of annular belts of equal resistance. The relation between the radii of successive equipotential circles with a constant difference of potential may be deduced from this condition as follows:—The resistance of any very narrow belt must be proportional to its breadth, or the difference between the radii of its external and internal circumferences; and it must be inversely proportional to the mean circumference, which, seeing that the circumference varies directly as the radius, will be simply the arithmetic mean of the external and internal circumferences. That is, if  $r_1, r_2, r_3$  are radii of successive circles, these circles

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will bound spaces of equal resistance if

$$\frac{r_2 - r_1}{\pi(r_2 + r_1)} = \frac{r_3 - r_2}{\pi(r_3 + r_2)},$$

or

$$r_1 r_3 = r_2^2.$$

Hence the radii of successive equipotential circles form a geometrical progression whose common ratio may be called  $\mu$ .

6. To find the resistance of a belt bounded by concentric circles whose radii are  $r_1$  and  $r_2$  respectively, let

$$\frac{r_2}{r_1} = \mu^n,$$

so that there are  $n$  equipotential circles contained in the belt, where

$$n = \frac{1}{\log \mu} \log \frac{r_2}{r_1}.$$

Denote the thickness of the conducting sheet by  $\delta$  and its conductivity by  $\kappa$ ; then, by the last section, the resistance of a narrow ring whose bounding circles have the radii  $l$  and  $l + \Delta r (= \mu l)$  will be

$$R_0 = \frac{1}{\kappa \delta} \cdot \frac{\Delta r}{\frac{1}{2}(2 + \Delta r) 2\pi} = \frac{1}{\pi \kappa \delta} \cdot \frac{\Delta r}{2 + \Delta r}.$$

But the whole belt we are considering is made up of  $n$  rings, each of the resistance  $R_0$ . So the resistance of the whole belt is

$$R = nR_0 = \frac{1}{(2 + \Delta r) \pi \kappa \delta} \cdot \frac{\Delta r}{\log(1 + \Delta r)} \log \frac{r_2}{r_1};$$

or, letting  $\Delta r$  decrease without limit,

$$R = \frac{1}{2\pi \kappa \delta} \log \frac{r_2}{r_1}. \quad \dots \quad (1)$$

7. Putting this value of  $R$  into the expression for the difference of potential of two circles of radii  $r_1$  and  $r_2$ , we have

$$V_1 - V_2 = \frac{Q}{2\pi \kappa \delta} \cdot \log \left( \frac{r_2}{r_1} \right),$$

whence the potential at any point of the sheet is at once given in terms of the strength of the source and the potential at unit distance from the source. Thus let  $V_1$  be the potential at unit distance, then the potential  $V$  at any distance  $r$  becomes

$$V = V_1 - \frac{Q}{2\pi \kappa \delta} \log r. \quad \dots \quad (2)$$

8. The same result may be obtained without previously cal-

culating the resistance of a belt of finite breadth as follows. The radii of successive equipotential circles, beginning at the pole itself, are (§ 5)

$$\mu^{-\infty} \dots \mu^{-2}, \mu^{-1}, 1, \mu, \mu^2 \dots \mu^{\infty}.$$

Let the common difference of potential between consecutive circles be  $\Delta v$ ; then, if  $r = \mu^n$ , the potential at distance  $r$  is less than the potential at unit distance by  $n$  times  $\Delta v$ , or

$$V_r = V_1 - n\Delta v = V_1 - \frac{\Delta v}{\log \mu} \log r.$$

But  $\frac{\Delta v}{\log \mu}$  is constant; and putting  $1 + dr$  for  $\mu$ , where  $dr$  is the breadth of the infinitely narrow belt whose inner boundary is the circle of unit radius, we have

$$\frac{\Delta v}{\log \mu} = \frac{dv}{\log(1 + dr)} = \frac{dv}{dr}.$$

Multiplying this by the circumference of the belt ( $2\pi$ ) and by the conductivity and thickness of the sheet, we get the strength of the current across the whole belt, or

$$2\pi\kappa\delta \frac{dv}{dr} = Q,$$

$$\frac{\Delta v}{\log \mu} = \frac{Q}{2\pi\kappa\delta},$$

whence

$$V = V_1 - \frac{Q}{2\pi\kappa\delta} \log r,$$

as before

### *Two equal Opposite Poles in an Infinite Sheet.*

9. If there are two or more electrodes in an infinite uniform conducting sheet, the strength and direction of the current and the potential at any part of the sheet are obtained by the simple superposition of the effects which each electrode would produce at that part if it were the only electrode in the sheet. This might be regarded as probable *à priori*; and it is proved by experiment to be the case. Hence the effect of any number of poles in a sheet may be deduced by properly extending the conclusions already arrived at with regard to a single pole. We will first discuss the case of a single source and a single sink of equal strength.

10. *Lines of Flow.*—Let A (Plate IX. fig. 1) be the source, and B the sink. The flow-lines due to these, taken separately, would be two equiangular pencils of straight lines drawn out-

wards from A and inwards towards B. These two systems of lines subdivide the whole surface of the conducting sheet into quadrilaterals, such as P Q and Q R. The actual direction of the flow at any point P, due to the combined action of the source and sink, will evidently be intermediate between the directions of the primary streams A P and P B through the same point; similarly the direction of the resultant current at Q will be intermediate between the direction of the primary streams A Q and Q B; in other words, the line of resultant flow through P will enter the quadrilateral P Q at P, and the line of resultant flow through Q will pass at Q from the quadrilateral P Q into the quadrilateral Q R. And it can be shown that the points P, Q, and R are points on the same line of flow—that is, that a continuous curve can be drawn through P, Q, and R such that no electricity flows across it. Thus, let the points of intersection of the primary flow-line A P with the primary flow-lines through B which are nearest to P B on either side of it, be marked P' and P<sub>1</sub> respectively; and similarly let Q' and Q<sub>1</sub>, R' and R<sub>1</sub> be the points where A Q and A R intersect the next flow-lines on either side of Q B and R B respectively. Then, since the total flow of electricity from A between the lines A P and A Q is everywhere the same and is equal to the flow towards B between the lines P B and Q B, which is likewise everywhere the same, the quantity of electricity flowing in a given time across any of the lines P Q', P<sub>1</sub> Q, P P<sub>1</sub>, Q' Q, which bound the quadrilateral P Q, is equal. Consequently, considering either of the triangles P Q' Q or P P<sub>1</sub> Q, the flow inwards across P Q' or P P<sub>1</sub> is equal to the flow outwards across Q' Q or P<sub>1</sub> Q; and therefore there cannot on the whole be any flow across a line drawn inside the quadrilateral from P to Q. Evidently also, by drawing a sufficient number of straight lines through A in directions intermediate between A P and A Q, and an equal number of lines through B in directions lying between P B and Q B, keeping the angle between consecutive lines constant in both cases, we can subdivide the line P Q into portions as short as we please, and such that no electricity flows across any of them. Hence P and Q are points on the same line of flow; and it follows, similarly, that the point R is also situated on this line. The same kind of reasoning also proves that a second line of flow passes through the points P', Q', and R', and a third through the points P<sub>1</sub>, Q<sub>1</sub>, and R<sub>1</sub>. Moreover, since the strength of the flow between the lines P' Q' R' and P Q R is measured by the quantity of electricity which in unit of time crosses any of the lines P' P, P Q', Q' Q, Q R', or R' R, and the strength of the flow between the lines P Q R and P<sub>1</sub> Q<sub>1</sub> R<sub>1</sub> is measured by the quantity which similarly crosses any of the lines P P<sub>1</sub>, P<sub>1</sub> Q, Q Q<sub>1</sub>,

$Q, R$ , or  $R R_1$ , and since these quantities are equal to each other, it follows that the lines  $P' Q' R'$ ,  $P Q R$ , and  $P, Q, R_1$  are consecutive flow-lines of a system which divides the conducting sheet into portions each of which conveys an equal current.

It is important to observe that the reasoning employed here is general, and not limited to the special case to which it has been applied. The general conclusion to which it leads may be thus stated:—If similar \* systems of lines of flow be drawn, corresponding to each of two separate systems of sources and sinks, the lines of flow which would result from the combined action of the sources and sinks of both systems will be obtained by drawing curves through the alternate angles of the quadrilaterals produced by the intersections of the two primary systems of flow-lines, in directions concurrent with both the primary flow-lines that intersect each other at each angle.

11. The method which, as we have seen, allows the flow-lines for two equal opposite poles to be drawn, also enables us to deduce very easily their general form. Let  $\alpha$  be the constant angle between consecutive flow-lines of the pencil diverging from A and of that converging to B. Then, evidently,

$$\angle A P B = \angle A Q B = \angle A R B = \dots = n\alpha,$$

where  $n$  is a constant integer. Also

$$\angle A P' B = \angle A Q' B = \dots = (n+1)\alpha,$$

and

$$\angle A P_1 B = \angle A Q_1 B = \dots = (n-1)\alpha.$$

Hence the lines of flow due to one source and one sink of equal strength are arcs of circles passing through the poles, each one differing from the next by a constant change ( $=\alpha$ ) in the angle which the radii vectores from the poles make with each other; or, what comes to the same thing, they are arcs of circles cutting each other at the poles with a constant difference of angle equal to the constant difference of angle ( $=\alpha$ ) between the rectilinear flow-lines which either the source or the sink would produce by itself.

12. The whole number of flow-lines is therefore  $\frac{2\pi}{\alpha}$ , or the same as the number of lines leaving the source or entering the sink when either of them is by itself in the sheet. This is evident also if we consider that infinitely near to either pole the effect of the other vanishes in comparison, and therefore the

\* By *similar* systems is here to be understood systems such that the total flow between any pair of consecutive lines of the one set is the same as that between any two consecutive lines of the other set.

lines close to each pole are the same in all respects as they would be if the other pole were absent.

13. The circular form of the flow-lines for the case we are considering can be demonstrated in various other ways. We will give here one additional proof, on account of its great simplicity.

The flow through any point P due to a source at A and a sink at B, being the resultant of the currents through the same point due to A and B taken separately, will be represented in strength and direction by the third side of a triangle whose other two sides represent the currents from A and towards B, respectively, in strength and direction. But the strengths of the two component currents are inversely as the distances AP and BP respectively (§ 4): hence the following construction (fig. 2). From B draw BT parallel to AP, and make its length a third proportional to AP and PB; then PT gives the direction of the flow at P, and its length is proportional to the strength of the current at P. The similarity of the triangles APB and PBT gives the angle BPT equal to the angle PAB; and consequently (converse of Euclid, III. 32) the locus of P is a circle through A and B.

14. It was shown in § 10 how a system of lines of flow can be traced out by successive points. To be able to draw them continuously with compasses we only require to know the position of the centres; and these are easily found from the following considerations. Since the circles of which the flow-lines are arcs pass through the poles A and B, their centres lie in the straight line at right angles to AB, through O its middle point. If C (fig. 3) be the centre of the circle which gives the flow-line through any point P, the angle at C is equal to the angle at P—the angle characteristic of the given flow-line; and therefore the angle OAC is the complement of the angle at P. Putting  $AB = 2a$ , we have

$$OC = a \cdot \tan OAC = a \cdot \tan \left( \frac{\pi}{2} - APB \right).$$

Let the number of lines to be drawn be  $m$ , then the constant difference between the angles contained under consecutive lines will be

$$\frac{2\pi}{m} = \alpha,$$

and the several lines will be given by making the angle at the circumference successively equal to

0,  $\alpha$ ,  $2\alpha$ , ...,  $\pi - \alpha$ ,  $\pi$ ,  $\pi + \alpha$ , ...,  $2\pi - 2\alpha$ ,  $2\pi - \alpha$ ,  $2\pi$ ,  
or, what is the same thing, to

$$0, \alpha, 2\alpha, \dots, \pi - \alpha, -\pi, -(\pi - \alpha), \dots, -2\alpha, -\alpha, 0,$$

where the values 0,  $\pi$ ,  $-\pi$ , and  $2\pi$  are represented by the straight line through A and B, and negative angles indicate flow-lines passing in the lower side of A B. But, as is evident from the figure, the same circle gives the two flow-lines whose characteristic angles are  $n\alpha$  and  $-(\pi - n\alpha)$ ; hence the number of circles to be drawn or of centres to be found is equal to half the number of flow-lines; and we need only consider those characterized by angles between 0 and  $\pi$ , of which the complements are

$$\frac{\pi}{2}, \frac{\pi}{2} - \alpha, \dots, \alpha, 0, -\alpha, \dots, -\left(\frac{\pi}{2} - \alpha\right), -\frac{\pi}{2}.$$

Consequently the required centres are obtained by drawing lines from A making the above angles with A B, and letting them intersect the perpendicular to A B through O; or, without measuring angles, by laying off from O in both directions along the perpendicular to A B lengths proportional to

$$0, a \tan \alpha, a \tan 2\alpha, \dots, a \tan \left(\frac{\pi}{2} - \alpha\right), a \tan \frac{\pi}{2}.$$

Plate IX. shows a system of lines of flow for which  $\alpha = 20^\circ$ .

15. The *strength of the current* at any point P due to a source at A and an equal sink at B is represented in the construction given in § 13 by the length of the line P T (fig. 2); but by the similarity of the triangles P B T and A P B,

$$\frac{P T}{B T} = \frac{A B}{P B};$$

or, putting  $A B = 2a$ ,  $B T = \frac{1}{r}$ , and  $P B = r'$ , the strength of the current is

$$s = \frac{Q}{2\pi} \cdot P T = \frac{Q}{2\pi} \cdot \frac{2a}{rr'}. \dots \dots (3)$$

Hence, for given poles at a given distance apart, the strength of the current is the same at all points of the sheet for which the product of the distances from the two poles is constant; or the loci of equal flow are a system of *lemniscates*\*.

\* The strength of the current at various parts of a circular disk with equal opposite poles on the edge was examined experimentally by Kirchhoff, by suspending a small magnet, with a mirror attached, close above the disk, and was found to agree closely with the results of calculation. Mach has since given a more direct proof that the lines passing through points of equal flow are lemniscates. A disk of silver-leaf was coated with a thin film of wax; and on allowing a strong current to traverse it for a few moments, the wax was melted within a space bounded by a lemniscate and the edge of the disk (Carl's *Repertorium f. experim. Physik*, vol. vi. p. 11, 1870).

16. *Equipotential Lines*.—The flow-lines for the case of one source and one equal sink having been determined, the form of the equipotential lines is at once given by the consideration that the two sets of lines cut each other orthogonally (§ 2); and it is a well-known geometrical result that the system of lines orthogonal to the system of circles which, as has been seen, represents the flow-lines for this case, is another system of circles having their centres on the line through the poles, each circle cutting this line once internally and once externally in points situated harmonically with respect to its extremities. The simplest general expression for such a system of circles is the equation

$$\frac{r}{r'} = c,$$

where  $c$  is a quantity which remains constant for each circle but varies from each circle to the next, and  $r$  and  $r'$  are the distances from any point of the curve to the source and sink respectively.

These general properties of the equipotential lines are easily established by referring to the construction employed in § 13. We there saw that  $PT$  (fig. 2) is a tangent to the line of flow through  $P$ ; and consequently it is normal to the equipotential line through the same point. If we produce  $PT$  to cut  $AB$  produced in  $C$ , we have the triangles  $BCP$  and  $PCA$  similar, and

$$CP^2 = CA \cdot CB;$$

whence it appears that if tangents to the lines of flow be drawn from any point  $C$  in  $AB$  produced, the distance from  $C$  to the points where these tangents touch the lines of flow is constant and depends only on the distances of the point  $C$  from  $A$  and  $B$  respectively. Therefore, if a circle be drawn with centre  $C$  and radius  $CP$ , it cuts all the lines of flow at right angles, and is consequently an equipotential line. If it is only required to find the centre of the equipotential circle through any point  $P$ , the simplest method is to make an angle  $BPC$  equal to the angle  $BAP$ ; then the point where  $PC$  and  $AB$  intersect is the centre to be found.

The similarity of the triangles  $BCP$  and  $PCA$  also gives

$$\frac{AP}{PB} = \frac{r}{r'} = \frac{AC}{CP};$$

or the ratio of the *radii vectores* from the two poles is constant for a given circle, as already stated.

17. The above method suffices for drawing the equipotential lines through any number of given points, but not for placing them *systematically* (or so that the difference of potential between consecutive lines may be constant). For this purpose we may



have recourse to a process of superposition of the same kind as that employed (§ 10) for placing the lines of flow.

We have seen (§ 5) that the equipotential lines for a single pole are concentric circles, and that the radii of consecutive circles form a geometrical progression. To find the system of equipotential lines for two equal opposite poles, it is only needful to draw for each pole separately a system of equipotential lines with the same difference of potential between any one line and the next as it is intended that there should be between the lines of the combined system, and then to draw lines through the intersections of the two overlapping systems of circles thus obtained, taking care, in going from one intersection to the next, that the changes of potential are in opposite directions for the two primary systems taken separately. Thus, let the lines 1, 2, 3, 4 (fig. 4) represent portions of equipotential lines due to a source at A; and 1', 2', 3', 4' portions of equipotential lines due to a sink at B; and let the potential of the line 1 be  $V$ , and let that of the line 1' be  $V'$ ; further, let the change of potential in passing from any one line to the next in either system be  $v$ , so that the potentials of the lines 2, 3, and 4 are  $V-v$ ,  $V-2v$ , and  $V-3v$  respectively, and the potentials of 2', 3', and 4' are  $V'+v$ ,  $V'+2v$ , and  $V'+3v$  respectively. Then, at the points where 1 and 1', 2 and 2', 3 and 3', 4 and 4' respectively intersect each other, the potentials will be the sums of the potentials of the intersecting lines; and therefore the potential at all these points is the same, namely  $V+V'$ . Consequently P, Q, R, and S are points on the same equipotential line. Similarly it follows that  $P_1$ ,  $Q_1$ , and  $R_1$  are points on the line whose potential is  $V+V'+v$ ; and  $Q'$ ,  $R'$ , and  $S'$  points on the line whose potential is  $V+V'-v$ . We thus get the potential of the resultant equipotential lines differing by the constant amount  $v$ , which is the same as the difference of potential of the lines of the two primary systems.

It is evident from this that any two systems of equipotential lines whatever, which have the same constant difference of potential, can be compounded, so as to give a single resultant system, by tracing lines through alternate angles of the quadrilaterals produced by the mutual intersection of the lines of the two systems, and also that the constant difference of potential between the lines of the resultant system will be the same as that between the lines of each of the component systems.

18. Let  $\mu$  be the common ratio of the radii of the equipotential circles of the two primary systems considered in § 17, and let the radius of the circle 1 be  $\mu^n$  and that of the circle 1' be  $\mu^m$  (see § 8); the radii of the successive circles of the one set are then  $\mu^{n+1}$ ,  $\mu^{n+2}$ , ..., and of those of the other  $\mu^{m+1}$ ,  $\mu^{m+2}$ , ...

Hence for the ratio of the radii vectores from the two poles for the points P, Q, R, S, we have

$$\frac{\mu^n}{\mu^m}, \frac{\mu^{n+1}}{\mu^{m+1}}, \frac{\mu^{n+2}}{\mu^{m+2}}, \frac{\mu^{n+3}}{\mu^{m+3}}$$

respectively; that is, we have for all these points the common ratio

$$\mu^{n-m}.$$

Similarly, we should find for the points P<sub>1</sub>, Q<sub>1</sub>, and R<sub>1</sub> the common ratio

$$\mu^{n-m+1},$$

and for the points Q', R', and S' the common ratio

$$\mu^{n-m-1}.$$

Hence, not only are the equipotential lines for two equal and opposite poles characterized by a constant ratio of the radii vectores, as already proved (§ 16), but this ratio *changes in a constant ratio* on passing from any one line of the system to the next, the ratio of change ( $=\mu$ ) being the same as the ratio of change of radius on passing from line of the system due to a single pole to the next.

19. The actual potential at any point of the sheet, in terms of the distances of this point from the two poles, follows directly from equation (2) in § 7. Let  $r$  be the distance of the given point from the source, and  $r'$  its distance from the sink; put  $V$  for the potential at the point due to the source alone, and  $V'$  for that due to the sink alone. Then we have

$$V = V_1 - \frac{Q}{2\pi\kappa\delta} \cdot \log r,$$

and

$$V' = V'_1 - \frac{Q'}{2\pi\kappa\delta} \cdot \log r';$$

and since the source and sink are equal,  $V'_1 = -V_1$  and  $Q' = -Q$ ; therefore the resultant potential, or  $V + V'$ , is

$$U = \frac{Q}{2\pi\kappa\delta} \cdot \log \frac{r'}{r} \dots \dots \dots (4)$$

This gives the potential  $= 0$  at all points of the straight line equidistant from the two poles, positive on the side of this line next the source, and negative on the side next the sink. Also it shows that for equal differences of potential we must have equal differences in the value of  $\log \frac{r'}{r}$ , which agrees with what was proved above (§ 18).

We may write (4) thus (§ 8),

$$U = \frac{Q}{2\pi\kappa\delta} \log \mu^n = n \cdot \Delta v ;$$

whence, regarding the source and sink for the present as mere points, the value  $n=\infty$  will correspond to the former, and  $n=-\infty$  to the latter, while  $n=0$  denotes the straight line at equal distances from both.

20. Let the distances from O (the middle point of A B) of the points D and D' (fig. 2), in which the circle of potential U cuts A B, be called  $l$  and  $l'$ ; then,  $a$  being as usual half the distance between the poles,

$$\frac{a+l}{a-l} = \frac{l'+a}{l'-a} = \mu^n,$$

where  $\mu^n$  is the ratio of the radii vectores of the given circle. Hence

$$ll' = a^2,$$

and

$$l = a \frac{\mu^n - 1}{\mu^n + 1}, \quad l' = a \frac{\mu^n + 1}{\mu^n - 1}.$$

For the radius of the circle, we have evidently

$$\rho = \frac{1}{2}(l' - l) = \frac{2a\mu^n}{\mu^{2n} - 1},$$

and for the distance of its centre from O,

$$d = l + \rho = l' - \rho = a \frac{\mu^{2n} + 1}{\mu^{2n} - 1};$$

also

$$\rho^2 = CA \cdot CB = (d+a)h = d^2 - a^2,$$

where  $h(=d-a)$  is the distance of the centre of the equipotential circle from the nearest pole.

21. In order to draw a system of equipotential circles with compasses, it is most convenient to have given the distances of the centres from the nearest pole, and also the distances from the same point of one of the intersections with A B, the line joining the poles—that is, in fig. 2 the distance B C and either B D or B D'. Now

$$BC = h = d - a = \frac{2a}{\mu^{2n} - 1},$$

$$BD = a - l = \frac{2a}{\mu^n + 1},$$

and

$$BD' = l - a = \frac{2a}{\mu^n - 1}.$$

Any convenient value such as 2 or  $\frac{3}{2}$  may be given to  $\mu$ ; or if a special number of lines be required, a value may be found to suit. Thus let  $L$  be the greatest value that is to be given to  $l$ , and  $m$  the number of lines required on each side of  $O$ . We shall have

$$\frac{a+L}{a-L} = \mu^m, \text{ or } \log \mu = \frac{1}{m} \log \frac{a+L}{a-L},$$

which determines the value of  $\mu$ .

The successive values of  $B D'$  are then

$$\frac{2a}{\mu-1}, \frac{2a}{\mu^2-1}, \frac{2a}{\mu^3-1}, \dots, \frac{2a}{\mu^m-1}.$$

The successive values of  $B C$  are simply alternate values of these, namely

$$\frac{2a}{\mu^2-1}, \frac{2a}{\mu^4-1}, \dots, \frac{2a}{\mu^{2m}-1}.$$

Plate IX. shows the equipotential lines drawn for a value of  $\mu = \frac{5}{3}$ .

[To be continued.]

#### XLV. Notices respecting New Books.

*The Principles of Science: a Treatise on Logic and Scientific Method.*

By W. STANLEY JEVONS, M.A., F.R.S., *Fellow of University College, London; Professor of Logic and Political Economy in the Owens College, Manchester.* London: Macmillan and Co. 1874 (two vols. 8vo, pp. 463 and 480).

THIS is in many respects a remarkable book, and particularly so in regard to the extraordinary number, variety, and (as far as we can venture to judge) accuracy of the facts which are brought in illustration of the principles and questions discussed. There is indeed scarcely a branch of science which the author has not laid under contribution for purposes of illustration. The work is divided into five books, viz.:—On Formal Logic, Deductive and Inductive; on Number, Variety, and Probability; on Methods of Measurement; on Inductive Investigation; and on Generalization, Analogy, and Classification.

We have found it very difficult to state in few words the upshot of the discussions in these books severally without doing great injustice to their contents. For instance, the first book might be said to be an exposition of formal logic designed to set forth the author's peculiar method of expressing propositions and arguments by symbols, and to lead up to an account of his logical machine—a machine worked by twenty-one keys like a pianoforte,

and able to draw inferences, or, at least, "to represent a mind endowed with powers of thought but wholly devoid of knowledge" (vol. i. p. 127). This, however, would be to give a very inadequate notion of the contents of this first part, though we do not see how to give a better account of it in few words. So, again, the second part might be said to contain an exposition of the doctrines of permutations and combinations, and of probabilities, which is closely connected with them, designed to lead up to the position that "we cannot adequately understand the difficulties which beset us in certain branches of science, unless we gain a clear idea of the vast number of combinations or permutations which may be possible under certain conditions. Thus only can we learn how hopeless it would be to attempt to treat nature in detail, and exhaust the whole number of events that might arise" (vol. i. p. 216). Yet this is not an adequate statement of the aim of Book II.; and the same would be found true of similar statements made in regard to the other books. Of course, in the case of any elaborate treatise the same may to some extent be true; but in the work before us the difficulty assumes unusually large dimensions, and renders the task of the reviewer peculiarly hard.

Probably the merit of the work lies mainly in the acute remarks which are freely scattered through it, and in discussions of particular points, which are often of great interest, and for the sake of which alone the work is well worth perusal. As an instance of this we will give a brief account of a single chapter (the twenty-sixth), which concludes the fourth book on "Inductive Investigation;" it is headed, "Character of the Experimentalist." After insisting on the impossibility that the efforts of many ordinary men should supply the place of the genius of exceptional men, and remarking that "nothing is less amenable than genius to scientific analysis and explanation," our author goes on to specify some of the mental characteristics of the natural philosopher. His mind must be readily affected by the slightest exceptional phenomena; his associating and identifying powers must be great; his imagination active; his powers of deductive reasoning sure and vigorous; and he must have so strong a love of certainty as to lead him to compare with diligence and candour his speculations with fact and experiment. It is sometimes thought that the philosopher will be cautious in following up trains of speculation; and the notion derives some countenance from the fact, that only successful trains of thought are commonly reserved for publication. But Mr. Jevons points out, from the examples of Kepler and Faraday, that, to use the words of the latter, "in the most successful instances not a tenth of the suggestions, the hopes, the wishes, the preliminary conclusions have been realized." He then considers the method pursued by Newton in the '*Principia*' and the '*Optics*' as a type of the true scientific method "of deductive reasoning and experimental verification." The chapter ends with a notice of a characteristic of the philosophic mind, to which we have never before had our attention so pointedly drawn, and which is well illustrated by

the example of Faraday, viz. the tenacity with which it will cling to a conception as likely to prove true and important in spite of repeated failures to verify it by experiment—which is of course a totally different thing from its being negatived by experiment. Thus Faraday first attempted to demonstrate a relation between magnetism and light in 1822; and though he frequently renewed the attempt, he was unsuccessful until, partly by accident, he obtained a result in 1845. In this case his tenacity was rewarded with success. Another series of attempts to demonstrate a reciprocal relation between gravity and electricity proved unavailing to the end. This instance very appropriately leads up to the remark, that “frequently the exercise of the judgment ought to end in absolute reservation,” the power to maintain this state being yet another characteristic of the philosophic mind.

In concluding our notice we will venture to do no more than to mention a single thought which has occurred to us several times while reading the work before us. It is this, that although given trains of reasoning, whether deductive or inductive, command universal assent, yet as soon as we get into a discussion of what constitutes the cogency of the reasoning, we are landed in the region of doubt and debate. This might be thought a paradox were it not so well known to be true. No one doubts the conclusiveness of the deductive reasoning by which Euclid proves his forty-seventh proposition; but let the question be started, What is deductive reasoning? and whence does it derive its conclusiveness? and we shall find the highest authorities giving different answers. A like remark applies to the far more complicated process by which the universal gravitation of matter is proved. Several of Mr. Jevons’s logical doctrines might be taken in illustration of these remarks; we will mention one or two.

1. Mr. Jevons, supported by high authority, regards the formula “Whatever is, is,” as a fundamental law of thought—though Shakspeare, to all appearance, regarded it as mere matter for a joke, and Locke treated its pretensions with scorn, and Mr. Mill thought the treatment just\*.

2. Mr. Jevons tells us (vol. i. p. 48) that “in ordinary language the verbs *is* and *are* express mere inclusion more often than not. ‘Men are mortals’ means that men form part of the class mortal.” There is, of course, a fundamentally different view of the case, according to which the word *is* merely predicates of men the

\* It might be supposed that the words “Whatever is, is,” mean “Whatever exists, exists;” but this is, apparently, not the case, its meaning being “*X* is *X*;” *e. g.* a circle is a circle, or, as Mr. Jevons put it, “a thing at any moment is perfectly identical with itself.” So that the clown in *Twelfth Night* seems to have understood the maxim when he said, “For as the old hermit of Prague, that never saw pen and ink, very wittily said to a niece of King Gorboduc, ‘That, that is, is;’ so I being master parson, am master parson.” The reference to Locke is Book IV. c. 7, of the ‘Essay concerning Human Understanding;’ that to Mr. Mill is p. 408 of ‘An Examination of Sir William Hamilton’s Philosophy.’

attributes of mortals—the fact of mortals forming a class being purely subsidiary and not necessarily coming into view at all.

3. We are told (vol. i. p. 136), “Neither in deductive nor inductive reasoning can we add a tittle to our implicit knowledge, which is like that contained in an unread book or a sealed letter. Sir W. Hamilton has well said, ‘Reasoning is the showing out explicitly that a proposition not granted or supposed is implicitly contained in something different which is granted or supposed.’” So far as the words “nor inductive” are concerned our author would, we suppose, stand nearly alone in his opinion. It is generally held that induction, or inductive inference, is a process that puts us in possession of something new; but when limited to deductive reasoning, the opinion expressed in the above sentence is very commonly held, though there are some who regard it as fundamentally erroneous. Suppose we took a full-grown man with perfect powers of reasoning, but wholly ignorant of geometry, there would be no difficulty in giving him a perfect knowledge of the definitions and axioms of the science. But when he came to prove the propositions of the first book (say the 47th) that would be quite another question, his success or failure would depend on his powers of invention. No working of the keys of any logical machine would put him up to the essential steps “through A draw AL parallel to BD or CE, and join AD, CF.” It certainly seems to us that considerations of this kind land us on this conclusion:—Either the first book of Euclid is not a specimen of deductive reasoning, or else the account commonly given of deductive reasoning is somehow or other erroneous. If we may venture on a surmise, we should say that the passage above quoted is couched in metaphorical language, and that the words “explicit” and “implicit” are used equivocally. To explicate is to unfold. We unfold a table-cloth when we put it on the table, we explicate the definition of a circle when we draw a learner’s attention to all the points involved—that it must be a plane figure, bounded by one line, &c. But, except by an improper use of language, we do not speak of an oak tree as being unfolded from an acorn; the oak tree is indeed derived from the acorn, but only by the continual assimilation of new matter. It is only in this latter sense, at least as it seems to us, that the first book of Euclid can be said to be unfolded from the definitions and axioms.

We have gone rather beyond our intention in the last paragraph, and will not venture further into the region of doubt and debate. We will therefore only add that, whether the student ends by adopting Mr. Jevons’s logical views or not, he will not fail to learn a great deal from an attentive perusal of this very able and comprehensive work.

*Introduction to Experimental Physics, Theoretical and Practical, including directions for constructing Physical Apparatus and for making experiments.* By ADOLPH F. WEINHOLD, Professor in the Royal Technical School at Chemnitz. Translated and edited, with the Author's sanction, by BENJAMIN LOEWY, F.R.A.S. With a Preface by G. C. FOSTER, F.R.S.

This is an elementary treatise on Experimental Physics which differs materially from those ordinarily used in our Schools and Universities. The object of the writer has been to present the general facts of elementary physics as plainly as possible, always in a concrete form, to keep abstractions as much as possible in the background, and to give instructions with such detail and minuteness as will enable the reader who is provided with simple tools and materials and endowed with a proper amount of patience, to make all the apparatus and perform all the experiments described in the book. These instructions are without doubt the most valuable part of the book, and constitute the feature by which it is distinguished from other elementary works on physics.

The subjects treated of are General Properties of Matter, General Mechanics and Mechanics of Solid Bodies, Mechanics of Liquid and Gaseous Bodies, Acoustics, Optics, Electricity, Magnetism, and Heat. To judge by the number of pages assigned to each of these subjects, they are considered of very unequal importance. While Heat is disposed of in 78 pages, as many as 316 are allotted to the Mechanics of solid and fluid bodies. The disproportion, however, is not so great as it seems, since of the latter many pages are occupied with a description of tools and methods of operating, which are as much employed upon apparatus for Heat as for Mechanics.

The study of Mechanics is introduced by an experimental investigation of the laws of falling bodies by Atwood's machine. This plan is one of which we cordially approve. An intelligent comprehension of the meaning of the term *force* is one of the most difficult to instil into the mind of a student. Usually an abstract definition of force is given in the beginning of the text-books which the student learns by heart; and not until he has worked his way through all manner of propositions involving the relations of forces does he learn the connexion between force and weight, how the weight of a body is a concrete expression of the attractive action of the earth upon it, and how forces are to be measured by the motional effects which they produce in bodies. It is a misfortune, however, that greater stress is not laid on the distinction between weight and mass, and also between force and acceleration. The term *mass* is introduced suddenly (p. 52) without any indication of the meaning it is intended to bear, and is frequently used as synonymous with *weight*.

The avoidance of abstractions and formulæ is sometimes carried to an excess. For instance, in the case of falling bodies, the ex-



periments are described which prove that the velocity attained when a particular force is acting is directly proportional to the time from the beginning of motion, that for a given mass moved the accelerations are as the forces which produce them, that for a given acceleration the spaces described are as the squares of the times, &c. The student finds that in 2, 3, 4 seconds the spaces are 4, 9, 16 times respectively the space described in the first second. But he is not invited to go beyond these particular cases, nor to find a general expression which shall apply to all his experiments. The formulæ  $s = \frac{1}{2}gt^2$ ,  $v = gt$ , &c., find no place in this book. Now, much as these and similar formulæ are abused by candidates for examinations, who learn them by heart and acquire a rule-of-thumb trick of applying them to problems without having any notion of their physical meaning, we do not think they should have been excluded from a work on elementary mechanics.

The principles of fluid-pressure are discussed and exemplified at great length; atmospheric pressure also and the barometer receive a good deal of attention: perhaps, however, a fuller description of the Aneroid Barometer might have been given with advantage. It is an instrument of such common use, that a brief account of the mechanism by which the motion of the lid of the box is transmitted to the index, and the mode of graduating the dial-face, would have been desirable.

The few pages devoted to the phenomena of air-suction, lateral pressure, Clement's disk and the spray-disperser are very lucid, leaving nothing to be desired in the way of explanation. The author's explanation of the phenomenon of the Clement's disk we will give nearly in his own words:—

“The effect of suction produced by a current of air is rendered especially obvious if the current is allowed to expand between two flat disks. A circular disk of cardboard 10 centims. in diameter has a hole in the middle. A glass tube about 8 millims. wide, bent at right angles, is passed through a cork which is glued upon the disk so that the bore of the tube is exactly over the hole in the disk. A second disk of stout paper or thin cardboard is suspended to the other by three threads; the distance between the disks should be 10 millims. If air is strongly blown through the tube it will expand between the plates in a radiating manner, and the particles of air will tend to move with the same velocity. But if the particles of air are to maintain the same velocity, then the same quantity of air which at any instant fills the space within the circle of 1 centim. radius will in the next instant have to fill the space within the ring of 2 centims. radius, in the next that within the ring of 3 centims. radius, and so on. If the particles of air are to maintain their original velocity, it is necessary that the quantity of air which at a certain time fills the inner circle of  $1 \times 3.14$  square centims. area, should fill at the following instant, the ring of  $(2^2 - 1) \times 3.14 = 3 \times 3.14$ , at the next instant the ring of  $(3^2 - 2^2) \times 3.14 = 5 \times 3.14$  centims. area, and so on;—that is, the

same quantity of air must successively fill a space 3, 5, 7, 9 times as great as at first, and must hence diminish its density and consequently its pressure so as to become from  $\frac{1}{3}$  to  $\frac{1}{9}$  of what it was in the centre of the circle. The pressure of the air which passes through the tube into the space between the disks is thus, although originally greater than the pressure of the atmosphere, gradually becoming less while radiating to, and escaping at the edge, and becomes actually less than the atmospheric pressure. It is true that the velocity of the air-particles decreases from the centre to the edge, and the diminution of pressure is not quite so great as would appear from our calculation, because the external air opposes a considerable resistance to the escaping current, but the ultimate effect is that the pressure over the greater portion of the space between the disks is less than the external pressure of the atmosphere: hence the remarkable result that the external air presses the suspended disk against the current blown from the tube, and moves it close to the fixed disk, and not until the current of air diminishes in strength will the disk fall back again."

The general principles of wave-propagation, both when the vibrations of the particles of the medium are transversal and also when they are longitudinal, are clearly explained, and a careful account given of the vibrations of strings, rods, and plates, the laws obeyed by them, the theory of overtones, &c. Occasionally, however, the explanations are by no means adequate: for instance, on page 382 we find the following, relative to the action of a flue organ-pipe:—"A current of air is directed through a narrow slit and strikes the opposite edge of the aperture or 'mouth' of the instrument." This is all: here the description comes to a sudden conclusion, while the reader is left to explain for himself as best he can what becomes of the air thus striking against the sharp edge, and how it sets in vibration the air-column in the pipe. A little further on, the pitch of an organ-pipe is spoken of as depending on its length only, the lengths of two open pipes which yield notes whose vibration-frequencies are as 2 to 1 being as 1 to 2. It might at least have been mentioned that the pitch is a function also of the cross section of the pipe.

On page 347 *pitch* and *tone* are used synonymously.

These, however, are small matters. On the whole the chapter on Acoustics is good, the portions relating to the organ of voice and the difference of vowel sounds of the same pitch as depending on the presence of various overtones, differing in intensity, combined with the fundamental, being especially well worked out.

In the Optics, after some well-considered directions have been given for the construction and silvering of mirrors, several simple cases of reflection are described and geometrically solved. There is here the same absence of general formulæ which we noticed in the case of the mechanics. The student is instructed to work out each example separately, and to determine geometrically the relative sizes of an object and its image and their distances from the mirror. No mention is made of spherical aberration (which the

experimenter cannot fail to notice and be perplexed by), nor, in the case of lenses, of chromatic aberration.

The student is taught how to make a spectroscope for himself which, though rough, is all that is absolutely necessary to show the distinctive spectrum-lines of such elements as sodium, lithium, calcium, &c. The description of this little apparatus, and of the method of using it, occupies many pages and is too long to quote here; it may, however, be stated that it consists of a single disulphide-of-carbon prism, which is made from the wider part of a lamp-cylinder cut obliquely at both ends and closed by glass plates, with an aperture on the upper side for pouring in the liquid. This is placed at one end of a long wooden box with square section, the further end of which is closed by a thin plate of wood with a narrow vertical slit in it. Following the directions given, the student will have no difficulty in arranging apparatus for exhibiting the reversion of the bright lines in the spectrum of an element, and in apprehending the cause of such reversion.

We find nothing about the phenomena of Interference or Diffraction. This is scarcely to be wondered at, since experiments on these subjects demand the use of more elaborate instruments than the author contemplates his students to be in possession of. His plan is throughout to confine himself to the exposition of such phenomena and principles as can be reproduced and exemplified by the student with such apparatus as he can construct for himself. The student is not expected to make measurements of any kind; he is not supposed to have arrived at such a state of proficiency in his subject. Indeed no measuring-instruments are described or even mentioned in any part of the book. We think, however, it would not have been inconsistent with the plan of the work had some of the elementary experiments on the polarization of light been given.

In the treatment of Electricity the same order is adopted as in the ordinary books on Physics. This portion of the work, not less than the rest, is characterized by copious illustration of principles and by many-sided hints and suggestions for insuring the success of the experiments described. In the main we agree with the writer of the Preface, that though the instructions may sometimes appear to readers unaccustomed to experimental work needlessly minute, yet it will appear in actual trial that the apparently small matters to which attention is sometimes called are just such as make the difference between success and failure. At the same time the thought forces itself upon us as we read through these many pages of instructions, that the author would have done wisely had he sometimes curtailed them, and so left space for many useful and important matters which he has been obliged to omit. We should like to have seen explained and illustrated the law of inverse squares as applied to electrical and magnetic attractions and repulsions, something about the torsion-balance, Faraday's theory of induction, specific inductive capacity, thermo-electricity, the tangent-galvanometer, electrical resistance, &c. Of none of these is any mention made.

The pages which treat of the magnetization of a rod of soft iron by a galvanic current and the attendant phenomena are well worth studying. The author explains clearly by a number of capital illustrations the Ampèrian theory of magnetism and the properties of solenoids. The applications of electromagnetism in telegraphy (Morse's Telegraph) and in the electric bell are well described. Considering, however, how much is omitted, nine pages are rather too many to devote to the electric bell alone.

In concluding this notice we may state our opinion that Weinhold's Introduction to Elementary Physics will prove of very great service to those who have to teach the elementary principles of Mechanics and Physics in schools, or otherwise, and are compelled by reasons of economy to construct their own apparatus; to these it will have the additional recommendation that the diagrams and pictures of apparatus are all drawn to scale, and the scale is in all cases given. We do not expect it will be largely adopted as a text-book in schools; it is too big and heavy, and too costly also.

#### XLVI. *Proceedings of Learned Societies.*

##### GEOLOGICAL SOCIETY.

[Continued from p. 329.]

June 10th, 1874.—John Evans, Esq., F.R.S., President,  
in the Chair.

THE following communications were read:—

1. "Notes on the Phenomena of the Quaternary Period in the Isle of Portland and around Weymouth." By Joseph Prestwich, Esq., F.R.S., F.G.S.

The author remarked that although the physical features connected with the later geological changes in this district were of much interest, they had hitherto attracted little attention. Commencing with the oldest drift-beds, he showed that the remains of one, formerly more extensive, had been found in the Isle of Portland at a height of 400 feet above the sea, that it contained the remains of the *Elephas antiquus*, *Equus fossilis*, &c., and that he found in this bed a number of pebbles of sandstone and ironstone of Tertiary age, and of chert from the Greensands—whence he inferred that, as such pebbles could not now pass over the plain of Weymouth, they must have done so before that area was denuded, and when bridged over by the Portland and Purbeck beds; for the pebbles are derived from beds which are only *in situ* to the north of the Weymouth district, and at a distance of 8 to 10 miles from Portland. Further this transport must have taken place before the elevation of the north end of Portland, and when the slope from the Bill to the Ridgeway was uniform and gradual. The anticlinal line which has elevated the intermediate area must be of later date than the drift-bed.

The author next proceeded to notice the raised beach at the Bill of Portland, in which he had, with the assistance of Mr. Jeffreys, determined 26 species of shells, two of them not now living in the British Channel, and one new. This beach contains pebbles of the Devonshire and Cornwall rocks.

The raised beach Mr. Prestwich found to abut against an old cliff that had been swamped at a later geological period by a land-wash, which had levelled it and the old sea-land with the adjacent land-surface. The mass which had thus swamped the cliff and buried the beach consisted of loam and angular débris, the latter being in larger proportion at top. In the loam he found several species of land and freshwater shells and fragments of bones. The angular débris consisted of pieces of the local rocks, together with a number of specimens which by their organic remains were shown to belong to the Middle Purbecks, a part of the series not now existing in Portland. A similar bed, but much thicker, was then described at Chesilton, in the north of the island. It is there 60 feet thick, and contains large blocks of Portland stone and Portland chert, the greater number of which are in the upper part of the deposit, which is here on the sea-level, and 400 feet lower than the Portland escarpment which rises above it. This loam and angular débris the author was disposed to attribute to a temporary submergence of the land to a depth exceeding the height of Portland, by which the land as it emerged was swept and its débris carried down to the lowest levels, with the remains of its land-animals and land and freshwater shells, which latter, where protected by large masses of loam and suddenly entombed, have been preserved uninjured. To this deposit, which is common over the raised beaches on the south coast, the author proposed to apply the term "Land-wash."

The paper concluded with a short notice of the drift-beds formed subsequently to the denudation of the Weymouth district, and therefore never on the high-level Portland drift. Among these was one near Weymouth of singular character, consisting almost entirely of subangular fragments of Greensand chert, which could not have been derived from beds nearer than Abbotsbury. The lower drift of the district is the valley-gravel of Upway and Radipole, in which the remains of *Elephas primigenius* have been found.

2. "On the Character of the Diamantiferous Rock of South Africa." By Prof. N. Story Maskelyne, F.R.S., F.G.S., Keeper, and Dr. Flight, Assistant, of the Mineralogical Department, British Museum.

In this paper the authors confirmed certain statements made by one of them from a superficial examination of specimens brought to this country by Mr. Dunn. The specimens examined and analyzed by Dr. Flight were obtained from various diggings and from different depths, down to 180 feet in the case of one mass from Colesberg Kopje. Their characters throughout are essentially the same.

The rock consists of a soft and somewhat pulverulent ground-mass, composed of a mineral (soapy to the touch) of a light yellowish

colour in the upper, and of an olive-green to bluish-grey colour in the lower parts of the excavations. Interspersed in the mass are fragments of more or less altered shale, and a micaceous-looking mineral of the vermiculite group, which sometimes becomes an important constituent of the rock, which also contains bright green crystals of a ferruginous enstatite (bronzite), and sometimes a hornblende mineral closely resembling smaragdite. A pale buff bronzite occurs in larger fragments than the green form of the mineral; and in the rock of Du Toit's pan an altered diallage is present. Opaline silica, in the form of hyalite or of hornstone, is disseminated through the greater part of the rock-masses; and they are everywhere penetrated by calcite.

The analyses of the component minerals (given in detail in the paper) show that this once igneous rock is a bronzite rock converted into a hydrated magnesium silicate, having the chemical characters of a hydrated bronzite, except where the remains of crystals have resisted metamorphism. Except in the absence of olivine and the small amount of augitic mineral, it might be compared with the well-known Lherzolite rock.

The diamonds are said to occur most plentifully, or almost exclusively, in the neighbourhood of dykes of diorite which intersect the hydrated rock, or occur between it and the horizontal strata through which the igneous rocks have been projected. The authors compare the characters of the diamonds found in different positions, and come to the conclusion that their source is not very remote from that in which they are now found.

The mineral above-mentioned as resembling vermiculite is described by the authors as a new species under the name of Vaalite.

## XLVII. *Intelligence and Miscellaneous Articles.*

### ON THE SPECTRUM OF THE AURORA.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

I WISH to point out a slight error in a communication from Mr. J. R. Capron on the Spectrum of the Aurora, which appears in the last Number of the Philosophical Magazine. Mr. Capron writes as follows:—

“From Dr. Watts’s ‘Index of Spectra’ I have extracted the three principal carbon-tube bands or lines; and they compare with Dr. Vogel’s oxygen-tube as under:—

	Yellow.	Green.	Blue.
Dr. Vogel’s oxygen-lines . . . . .	5603	5195	4834.
Dr. Watts’s carbon-tube bands or lines.	5622	5189	4829

“The 5622 for the yellow line of the tube must be an error. 5608 seems to me, from my own observations, nearer its place; and I calculate 5193 and 4825 for the other lines.”

The number 5622 Mr. Capron has taken by mistake from the wrong series of numbers—from spectrum No. I. instead of from spectrum No. II. The other two numbers, 5189 and 4829, I am not able to find in the ‘Index of Spectra’ at all. The wave-lengths actually given for the three lines of the *tube*-spectrum are as follows:—

Spectrum No. II.

<i>j</i> 58 .....	5602
<i>k</i> 74 .....	5195
<i>l</i> 92 .....	4834

I have satisfied myself that these lines are due to a *compound* of carbon and *oxygen*; and their production in tubes supposed to contain oxygen is not at all surprising. The results obtained by the use of vacuum-tubes must always be received with caution, since it is almost impossible to form any certain conclusion as to the real nature of the small quantity of gas remaining in the tube, even when one has filled the tube one’s self; and in the case of tubes purchased from makers of such apparatus, the nature of the contents is simply a matter of conjecture.

I am, &c.,

W. MARSHALL WATTS.

Giggleswick Grammar School,  
April 14, 1875.

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EXPERIMENTS WITH THE HOLTZ MACHINE. BY F. ROSSETTI\*.

In a recent series of experiments upon the Holtz machine, first pattern, M. Rossetti sought to determine in what measure the intensity of the current produced depends on the velocity of rotation of the machine, on the work expended, and on the humidity of the air, to estimate its electromotive force, internal resistance, &c. The results at which he arrived on these points are the following.

In one and the same series of experiments, the intensity of the current is very sensibly, but not exactly, proportional to the velocity of rotation of the plate; the intensity increases a little more rapidly than the velocity of rotation.

The effect is modified by the humidity of the air, the velocity necessary to produce a certain intensity being greater in wet than in dry weather.

The work expended for the production of the electricity is exactly proportional to the intensity of the current. It was measured by the difference of the weights necessary to impress a certain velocity on the plate, according to whether the machine was charged or not.

\* *Nuovo Cimento*, Ser. 2, vol. xii. p. 89.

The ratio between the work expended and the intensity of the current diminishes when the humidity augments—in such a manner that, to obtain a current of given intensity, a greater velocity of rotation is requisite in wet than in dry weather, but a less expenditure of work. The Holtz machine is therefore more economical in wet weather than in dry.

The distance between the two disks of the machine has also some influence on the intensity of the current: the less the distance the stronger the current, and the greater the amount of the work.

The Holtz machine, like the voltaic couples, possesses electromotive force and internal resistance. The electromotive force is independent of the velocity of rotation; but it diminishes as the degree of humidity increases. The effective motor weight (difference between the weights necessary to turn the machine charged and not charged) is proportional to the electromotive force produced. This is very great in comparison with the electromotive forces of the most energetic voltaic couples; in fact it has been found to amount to 433000 Siemens units with a relative humidity equal to 0.69, to 599000 with the humidity 0.35—the Daniell couple giving  $E=11.57$ , and that of Grove  $E=19.98$ . The electromotive force of the Holtz machine is therefore about 50000 times as great as that of the Daniell couple, and 30000 times as great as that of the Grove couple.

The internal resistance of the Holtz machine is independent of the hygrometric state, but varies with the rotation-velocity, diminishing more rapidly than the velocity increases. It is very great: the lowest resistance (which corresponds to the greatest velocity attainable, or 8 turns per second) is equal to 570 million Siemens units; for a velocity of 2 turns per second it is 2810 millions of the same units.

Under these conditions a resistance inserted in the outer circuit must be very considerable in order to exert any sensible influence on the intensity of the current. It was because the resistance employed by Poggendorff was too feeble that he could not verify an effect of this kind. M. Rossetti, on the contrary, by interposing in the circuit a column of distilled water of greater or less length, has ascertained that the current of the Holtz machine is susceptible of being very notably weakened by augmentation of the external resistance, following Ohm's law in this equally well with the ordinary galvanic currents.

The author has deduced from his experiments a measure of the mechanical equivalent of heat, by comparing the serviceable work expended for the production of the electricity with the total heat which could be developed by the current obtained. He found for that equivalent the number 428.—*Bibliothèque Universelle, Archives des Sciences*, March 15, 1875, pp. 250–252.



ON THE SOLUTION OF HYDROGEN IN METALS, AND THE DECOMPOSITION OF WATER BY IRON. BY MM. L. TROOST AND P. HAUTEFEUILLE.

In previous researches on the alloys formed by hydrogen\*, we have pointed out the characters by which these definite combinations may be distinguished from the solutions of hydrogen in the metals. We have seen that besides potassium, sodium, and palladium, which can combine with hydrogen, there are other metals which simply dissolve this gas. The number of those which possess this last property appears to be considerable.

We shall see that iron, nickel, cobalt, and manganese, which are united by the analogy of their chemical properties into a natural group, present great similarities in their behaviour in the presence of hydrogen at various temperatures. As the facility with which they absorb or give out hydrogen depends largely on their physical state, it is necessary, in order to account for the differences observed, to investigate these metals successively in ingots, in thin plates, and in the pulverulent condition.

I. *Nickel*.—An ingot of pure nickel, cast in lime, was submitted for twenty-four hours, at a red heat, to the action of a current of hydrogen gas, and then cooled slowly in the gas. The volume of hydrogen extracted from it at a red heat *in vacuo* was one fifth of the volume of the metal.

Some laminæ of nickel, obtained by decomposing with the pile the double sulphate of nickel and ammonia, were heated in a vacuum to 200° C.; they gave out forty times their volume of hydrogen†. On afterwards being heated to near 200° in a current of hydrogen and slowly cooled in this gas, they absorbed sixteen times their volume of it, which they gave up *in vacuo* at 200°. The same laminæ, placed for twenty-four hours at the negative pole of a voltmeter, absorbed about ten times their volume of hydrogen‡.

The pulverulent nickel was obtained by reducing the oxide or a mixture of oxide of nickel and alumina by means of hydrogen at 300°. Nickel thus prepared is pyrophoric, as Magnus has shown§. In a vacuum it gives up a certain quantity of hydrogen at the ordinary temperature; but to expel this gas entirely a dull red heat is requisite. The total volume of gas discharged is about one hundred

\* *Comptes Rendus de l'Acad. des Sciences*, vol. lxxviii. pp. 686, 807. *Phil. Mag. S. 4.* vol. xlvii. p. 397.

† The gas analyzed did not give any perceptible quantity of nitrogen. Some laminæ prepared in the same way, then washed and dissolved in chlorhydric acid, gave traces of ammonia.

‡ M. Raoult states (*Comptes Rendus*, vol. lxi. p. 826) that the impure porous nickel cubes of commerce, when placed at the negative electrode of a voltmeter, absorb 165 volumes of hydrogen, which they gradually disengage at the ordinary temperature. The same cubes electroplated with pure nickel did not appear to him to disengage any appreciable quantity of gas.

§ *Annales de Chimie et de Physique*, 2 série, vol. xxx. p. 103.

*Phil. Mag. S. 4.* Vol. 49. No. 326. May 1875. 2 F

times that of the metal. Submitted, at a dull-red heat, to the action of a current of hydrogen, it reabsorbs a volume sensibly equal to that which it had discharged. The metal is again pyrophoric after the hydrogen is expelled.

II. *Cobalt*.—An ingot, cast in lime, of pure cobalt was submitted to a red heat for twenty-four hours in a current of hydrogen, and then cooled slowly in that gas. The volume of hydrogen extracted from it *in vacuo* at a red heat was only one tenth of that of the metal.

Laminæ of cobalt, obtained by galvanic decomposition of the double sulphate of cobalt and ammonia, were heated *in vacuo* to 200°. They gave up thirty-five times their volume of hydrogen\*. Heated subsequently in a current of hydrogen to about 200°, and again cooled slowly in the same gas, they absorbed twenty-four times their volume of it, which they set free again *in vacuo* at 200°. The same laminæ, placed during twenty-four hours at the negative pole of a voltameter, absorbed seven times their volume of hydrogen.

Pyrophoric cobalt loses its hydrogen *in vacuo* still more readily than nickel. Instead of making a vacuum, the condensed gas can be expelled by putting the metal into a small balloon furnished with a discharge-tube and filled with water exhausted of air. Heated to 100°, all the gas is disengaged in a few hours. The volume of the gas thus collected is about one hundred times that of the metal; the cobalt, too, is again pyrophoric after complete expulsion of the hydrogen. Submitted at a dull red heat to the action of a current of hydrogen, it reabsorbs a volume equal to that which it has set free.

III. *Iron*.—We have previously proved† that 1 kilogramme of soft iron in the form of an ingot can dissolve at about 800°, and afterwards set free *in vacuo* at the same temperature, 20 cubic centims. of hydrogen, or one sixth of its own volume. Under the same conditions 1 kilogramme of grey pig-iron, wood-cast, dissolves 88 cubic centims. of hydrogen, or more than the half of its volume‡.

It is known that the iron obtained in decomposing by the pile chloride of iron in the presence of sal ammoniac, when plunged into hot water disengages hydrogen and at the same time a small quantity of ammonia, as was proved by MM. Meidinger§ and Kroemer||. M. Cailletet¶ has recently obtained in this way a volume of hydrogen equal to 260 times that of the metal.

\* Analysis of the gas did not show any sensible quantity of nitrogen. Some laminæ prepared in the same manner, then washed and dissolved in chlorhydric acid, gave, like the nickel, traces of ammonia.

† *Comptes Rendus*, vol. lxxvi. p. 562.

‡ We have since ascertained that iron wire, hardening slightly by steeping, dissolves at a red heat nearly one fourth of its volume of hydrogen; the same wire, after cementation, dissolved one third of its volume of the gas. The solubility of hydrogen in steel increases, therefore, with the amount of carbon contained in the latter.

§ *Dingl. Polytech. Journ.* vol. clxiii. p. 283.

|| *Arch. Pharm.* 2nd Series, vol. cv. p. 284.

¶ *Comptes Rendus*, vol. lxxx. p. 319.

Pyrophoric iron obtained by reducing at a low temperature either the sesquioxide alone or a combination of oxide of iron and alumina (precipitated from their chlorides by ammonia), gives up, like pyrophoric nickel and cobalt, all its hydrogen *in vacuo*, and, like them, retains the property of ignition at a low temperature in air. As to the quantity of hydrogen which can be fixed by pyrophoric iron, its determination presents special difficulties. The cold metal loses *in vacuo* a portion of the gas which it absorbed. Boiling water, by the use of which we succeeded in obtaining the hydrogen dissolved in pyrophoric nickel or cobalt, gave with iron entirely different results. In fact, the pyrophoric iron which comes from the reduction of the combined oxides of iron and aluminium, put with air-exhausted water into a small balloon furnished with a discharge-tube, gave a continuous disengagement of hydrogen when heated: thus 1 grm. of iron liberated 10 cubic centims. of gas per hour; and the liberation went on until the iron was almost completely oxidated. The water was therefore decomposed at about  $99^{\circ}$  by the minutely divided iron. Pyrophoric iron from the reduction at a low temperature of the hydrate of the sesquioxide alone, decomposes water with a rapidity nearly equal to that of the metal combined with alumina.

With respect to the pulverulent iron less minutely divided which is obtained on reducing by hydrogen the sesquioxide resulting from the calcination of the nitrate, it also decomposes water at about  $99^{\circ}$ , but the decomposition is much slower. The reduced iron of commerce and the spongy iron obtained by the galvanic pile behave in the same manner\*.

Not being able to determine by immersion in boiling water the volume of the gas condensed in pyrophoric iron, we essayed to determine it by keeping the iron in cold water; but here again we had to recognize the decomposition, though slower, of the water: 1 gramme of pyrophoric iron, kept in water deprived of air and at  $15^{\circ}$ , liberated hydrogen regularly during two months.

In brief, iron, nickel, and cobalt directly absorb hydrogen; but we cannot affirm that combination takes place: this is what we have already proved for lithium and thallium. Pyrophoric iron, nickel, and cobalt condense a greater quantity of gas than the compact metals; but the whole of the gas is liberated below a red heat, and the metals deprived of hydrogen continue to be pyrophoric: this property therefore does not depend on the presence of condensed hydrogen. Finally, iron in a state of minute division exhibits a property which is not found in either nickel or cobalt; it decomposes water slowly at ordinary temperatures, and rapidly at about  $100^{\circ}$ : in this respect it approaches manganese, of which we shall shortly make known some new properties.—*Comptes Rendus de l'Acad. des Sciences*, vol. lxxx. pp. 788–791.

\* The vapour of water, under the tensions comprised between 5 and 25 millims. is likewise decomposed by iron at the temperature of  $100^{\circ}$ , as results from experiments by H. Sainte-Claire Deville.

ON A LECTURE-ROOM APPARATUS FOR THE DETERMINATION OF  
THE MECHANICAL EQUIVALENT OF HEAT. BY H. J. PULUJ,  
ASSISTANT IN THE IMPERIAL MARINE ACADEMY, FIUME.

The apparatus is of very simple construction, consisting essentially of a calorimetric and a dynamometric portion, suitably connected with an oscillation-machine such as is found in every physical cabinet.

The calorimetric part is formed by two hollow truncated cones of cast iron, one fitting into the other, the inner not quite reaching to the bottom of the outer, and appearing a little outside of it. The outer cone can be fixed coaxially in the vertical bobbin of the machine. The inner cone contains mercury. If the machine is put in motion and the inner cone fixed, heat is generated by the friction of the surfaces.

An arrangement which is an inversion of Prony's check serves for the measurement of the work which is converted into heat. On the wooden lid of the inner cone a light wooden beam is screwed horizontal. A perforation passing through the beam and lid receives the thermometer. At some distance from the beam is a fixed pulley on a level with it, over which a thread, to which a scale is suspended, is slung and is fastened to the end of one arm of the beam; the other arm serves as a counterpoise. When the machine is set in motion, the interior face of the outer cone rubs against the surface of the inner one, and tends to turn the beam which is fastened to the latter in the direction of the motion. With a certain load the horizontal part of the thread and the axis of the beam will include a right angle. From the length of the beam-arm, amount of the load, and number of rotations the work converted into heat, and from the water-value of the calorimeter and the rise of temperature the quantity of heat generated, can be calculated.

The memoir contains also the development of the theory of the apparatus, taking into consideration the heat radiated from the calorimeter, and, finally the numerical calculation of the values of the mechanical equivalent of heat from 28 experiments. The mean of those numbers, 425.2, with the mean error  $\pm 5.4$ , is in excellent accordance with Joule's result, 424.9, and may be regarded not only as a fresh corroboration of it, but also as a measure of the accuracy with which the experiments can be conducted by means of this simple apparatus; and these occupy but very little time, an experiment proper lasting but 30–60 seconds, on which account the apparatus may be recommended for lecture-experiments.—*Kaiserl. Akad. der Wissenschaften in Wien, math.-naturw. Classe*, April 15, 1875.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FOURTH SERIES.]

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JUNE 1875.

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XLVIII. *On the Electric Conducting-power of the Chlorides of the Alkalies, Alkaline Earths, and Nitric Acid in Aqueous Solutions.* By F. KOHLRAUSCH and O. GROTRIAN\*.

THIS memoir is to form the commencement of a systematic experimental investigation of the work of the current in the interior of electrolytes. In order to arrive at laws in this obscure department, the first requisite is a detailed inquiry into the facts. For the materials we possess are very imperfect, and for the most part inexact; and the measurements, with few exceptions, have not been referred to a sufficiently defined unit; so that up to the present only a slender basis is afforded for more general points of view. Thus much, however, is already known, that the relations are by no means simple; and accordingly, in order to analyze them, it will be advisable to commence with simple chemical combinations and examine these in groups.

On this account we have operated first upon the chlorides of the alkalies and alkaline earths. The observations refer to thirty-five different solutions of them, and show the dependence of the conducting-power on the amount of salt contained, and on the temperature from  $0^{\circ}$  to  $40^{\circ}$  C. Chloride of lithium is the only one that was examined merely in very dilute solutions.

Of the acids, we have previously experimented on sulphuric and hydrochloric†. We now add nitric acid, about the electri-

\* Translated from an abstract, communicated by the Authors, in the *Nachrichten von der königl. Gesellschaft der Wissenschaften zu Göttingen*, No. 17, August 5, 1874.

† *Nachrichten*, 1868, p. 415; *Pogg. Ann.* vol. cli.  
*Phil. Mag. S. 4.* Vol. 49. No. 327. June 1875.

city-conducting power of which almost nothing was known. Observations have been made on it in seven proportions of solution; and thereby a sufficient knowledge for all purposes has been gained.

The method used for measuring the resistances was the one first described in the *Nachrichten* (1869, Nov. 14)—that of quickly alternating currents, which, with some subsequent improvements (namely, the production of a convenient induction-coil for the alternating currents, the application of Wheatstone's bridge to the dynamometer, and the introduction of platinized electrodes\*), in simplicity and accuracy leaves nothing to be desired. Indeed the determination of the temperature of the liquid under experiment now presents greater difficulties than the measurement of the resistance, if the same degree of accuracy is demanded for both.

We have been most careful to make sure of the sensibly complete exclusion of polarization of the electrodes, which, when constant currents were used, hindered the exact measurement of the work of the current in decomposable conductors. To mention one of the tests applied in this direction, we experimented upon a solution of sulphate of zinc, first between electrodes of amalgamated zinc (which generally give no polarization), and then between the platinized platinum electrodes of 2000 square millims. surface which were employed for all the subsequent measurements. The greatest difference between the resistances found corresponded to a temperature-error of about  $\frac{1}{40}$  of a degree. With the zinc electrodes, constant as well as alternating currents were used; and at the same time, by the accordance between the results, it was established that the work of the alternating currents follows the same laws as that of a constant current.

From the commencement onward, the materials for observation were so arranged as to facilitate comparison when put together in Tables. The solutions contained approximately 5, 10, ... (or, in the case of nitric acid, 6.2, 12.4, ...) per cent.; and the temperatures were near 0°, 18°, and 40°; so that reduction to exactly these proportions was attended with no risk of error.

Our thanks are due to Professor Büchner, Dr. Heumann, and Dr. Rössler for the preparation and analysis of the most concentrated solutions of each substance. The other solutions were prepared from these by weight.

The specific gravities (at 18°; water at 4° equal 1) present a second definition, independent of the analysis, of each solution.

The electric conducting-powers  $k$ , given below, are all referred to that of mercury at 0° as unity. Siemens's standards no. 1135 and no. 1143, which were made use of for the reduction of the

\* Pogg. *Ann.* Jubelband, p. 290, vol. cli. p. 378.

mercury unit to absolute measure†, served for this reduction. The resistance of a column of liquid of 1 square millim. base and 1 millim. length, is found to be, in absolute measure,  $= \frac{9717000 \text{ millim.}}{k \text{ sec}}$ . This, in  $\frac{\text{millim.}^2 \cdot \text{milligr.}}{\text{sec.}^2}$ , is at the same time the work of the unit current which passes this column in a second.

Scarcely any property of bodies depends to so great a degree upon the temperature as the conductivity of electrolytes, which at middle temperatures is influenced as much as ten times as powerfully by heat as the pressure of a gas. On this account observations of the resistance without statement of the temperatures of liquids possess but little value.

But even apart from this, the influence of temperature is here of singular importance, precisely on account of its unusual magnitude; for it follows that the electro-chemical work of the current stands in intimate relation with the thermal condition of the liquid, the tracing-out of which relation may supply an invaluable explanation on the nature of electrolysis. We have comprehended the observations of each solution in the formula

$$k_t = k_0(1 + \alpha t + \beta t^2),$$

in which  $k_t$  signifies the conductivity at temperature  $t$ .

Besides these constants  $k_0$ ,  $\alpha$ , and  $\beta$ , the following Table contains the conducting-power at  $18^\circ$  multiplied by  $10^8$ , and, finally, under  $\left(\frac{1}{k} \frac{dk}{dt}\right)_{18}$ , the increment for  $1^\circ$  in the vicinity of  $18^\circ$ , expressed in fractions of the conducting-power at  $18^\circ$ .

The percentages denote parts by weight of anhydrous salt, or of nitric-acid hydrate, in parts by weight of the solution. The specific gravities are for  $18^\circ$ .

The solutions marked with an asterisk (\*) have not been analyzed; but their content was taken, according to the specific gravity, from R. Hoffmann's *Tabellen für Chemiker*. The conducting-powers &c. set down for the bracketed percentages were interpolated from a graphic representation of the results, and are here and there uncertain to a few units in the last place. The most concentrated solution of  $\text{NH}_4\text{Cl}$  precipitated some crystals at  $0^\circ$ , when a leap in the conducting-power was not observed. Two solutions of  $\text{MgCl}_2$  were examined only at  $18^\circ$  and  $30^\circ$ ; and two of  $\text{SrCl}_2$ , at  $18^\circ$  only. The strongest nitric contained a little nitrous acid.

† *Nachrichten*, 1870, p. 513. It is not unimportant to remark that the present comparison of the two standards gave, to within  $\frac{1}{80000}$ , the same ratio as that made four years previously.

Per cent.	Specific gravity.	$10^8 k_0$ .	$\alpha$ .	$\beta$ .	$10^8 k_{18}$ .	$\left(\frac{1}{k} \frac{dk}{dt}\right)_{18}$ .
NaCl.						
5	1.0346	402	0.0292	+0.000110	628	0.0212
10	1.0710	729	290	102	1132	212
15	1.1089	998	279	110	1535	207
20	1.1482	1177	290	108	1830	211
24	1.1802	1239	311	111	1979	220
KCl.						
5	1.0309	426	0.0271	+0.000078	645	0.0198
10	1.0639	865	249	065	1271	186
15	1.0978	1313	233	058	1889	177
21	1.1410	1873	217	039	2628	165
LiCl.						
5	1.0274	431	0.0308	+0.000110	685	0.0218
10	1.0562	731	288	118	1139	212
NH <sub>4</sub> Cl.						
5	1.0142	572	0.0266	+0.000074	859	0.0195
10	1.0289	1139	242	068	1661	183
15	1.0430	1711	221	053	2419	169
20	1.0570	2251	218	019	3147	161
25	1.0724	.....	.....	.....	3765	155
CaCl <sub>2</sub> .						
5	1.0409	386	0.0292	+0.000093	601	0.0209
10	1.0853	700	274	094	1067	202
(15)	1.1312	940	.....	.....	1407	197
20	1.1795	1078	260	094	1616	196
25	1.2306	1095	275	082	1665	200
30	1.2843	1009	273	138	1550	210
35*	1.3420	793	309	164	1277	229
MgCl <sub>2</sub> .						
5	1.0416	404	0.0297	+0.000123	639	0.0217
10	1.0861	664	300	106	1048	215
(15)	1.1295	.....	.....	.....	1250	220
20*	1.1765	.....	.....	.....	1311	230
(25)	1.2257	.....	.....	.....	1220	247
30*	1.2780	570	367	305	992	270
34	1.3212	.....	.....	.....	713	303
BaCl <sub>2</sub> .						
5	1.0446	234	0.0291	+0.000097	364	0.0209
10	1.0940	448	279	084	686	202
15	1.1475	654	264	087	983	196
(20)	1.2051	833	.....	.....	1239	192
24	1.2564	972	249	082	1435	189
SrCl <sub>2</sub> .						
5	1.0443	290	0.0293	+0.000098	452	0.0210
10	1.0931	544	273	104	829	203
15	1.1456	.....	.....	.....	1151	.....
(20)	1.2023	.....	.....	.....	1398	.....
22	1.2259	.....	.....	.....	1480	.....
HNO <sub>3</sub> .						
6.2	1.0346	2118	0.0218	-0.000037	2924	0.0148
12.4	1.0717	3731	204	-0.000025	5072	143
(18.6)	1.1105	4830	.....	.....	6460	138
24.8	1.1525	5402	184	-0.000003	7185	138
31.0	1.1946	5462	190	-0.000008	7319	140
37.2	1.2372	5206	198	-0.000001	7062	146
(43.4)	1.2786	4790	.....	.....	6550	152
49.6	1.3190	4274	212	+0.000020	5935	158
(55.8)	1.3560	3770	.....	.....	5290	161
62.0	1.3871	3296	232	-0.000027	4646	158



The dependence of the conducting-power of the chlorides on the temperature shows, according to the above, great simplicity in many respects. The universally small amount of the coefficient  $\beta$  proves that, with all solutions, *the conducting-power increases in nearly equal proportion with the temperature*; the positive sign of  $\beta$ , that *each of the slight deviations consists of an acceleration*.

With so strongly pronounced a dependence as we have here (with which  $30^\circ$  rise of temperature about doubles the conducting-power), this nearly equal proportional augmentation could not *a priori* be expected. It has, however, been observed also in sulphate-of-zinc and sulphuric-acid solutions\*, and appears to be a universal property of liquid conductors. Viscous substances only, such as concentrated solutions of chloride of calcium, chloride of magnesium, and sulphuric acid, exhibit greater inequality.

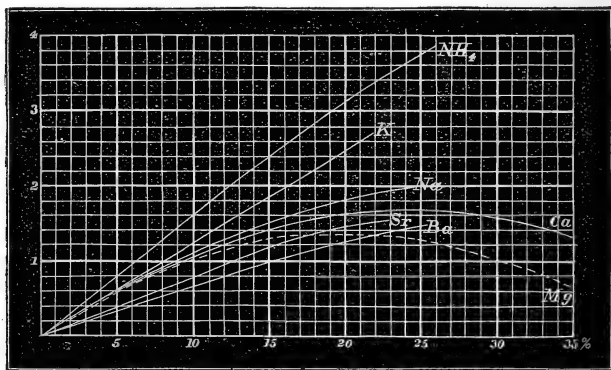
A further, very remarkable fact is *the near approximation to equality of the temperature-coefficients for the different chlorides in dilute solution*. Those at  $18^\circ$ , for example, for all 5-per-cent. solutions, lie between  $\frac{1}{48}$  (for LiCl) and  $\frac{1}{32}$  (for  $\text{NH}_4\text{Cl}$ ); the graphic representation permits the conjecture that with further dilution they would come still nearer together; nay, it is probable that they tend to the same limit (about  $\frac{1}{43}$ ). And certainly this limit cannot signify the temperature-coefficient of pure water, since the conducting-power of this is generally a vanishing quantity in comparison with the numbers in the above Table. The temperature-coefficient of sulphate-of-zinc solution, too, observed by Beetz, appears as the dilution is increased to approach towards about the same limit.

*With increasing amount of salt contained, all the temperature-coefficients at first diminish*. Afterwards the substances divide themselves into two groups: KCl,  $\text{NH}_4\text{Cl}$ , and  $\text{BaCl}_2$  show a diminution of the coefficients up to the greatest concentration, the coefficient sinking in the case of  $\text{NH}_4\text{Cl}$  to the lowest value,  $\frac{1}{64}$ . NaCl,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ , on the contrary, have a minimum between 10 and 20 per cent.; and thence onward the coefficient rises, that of  $\text{MgCl}_2$  even to  $\frac{1}{33}$ . This group-difference appears to be connected with a maximum of conducting-power with the salt-content, exhibited by the latter substances, but not by the former. (Compare what is stated below.)

Nitric acid connects itself with the latter group. In the sign of  $\beta$  changing from  $-$  to  $+$  it agrees with sulphuric acid; yet the inequality of the augmentation between  $0^\circ$  and  $40^\circ$  is generally slight. The absolute amount of the influence of temperature is less than with the chlorides, and not very different from that observed with hydrochloric and sulphuric acids.

\* Beetz, Pogg. Ann. vol. cxvii. p. 21; Grotian, *ibid.* vol. cli. p. 394.

If we now consider, secondly, *the dependence of the conducting-power on the amount of salt or acid contained*, the only thing common to all the substances investigated appears to be the *constancy of the variation*. The annexed figure exhibits this better than the numbers in the Table. It has for abscissæ the percentage contents, and for ordinates the conducting-powers at  $18^\circ$ . LiCl, so far as it was investigated, very nearly coincides with NaCl, and is therefore not delineated.



Both the absolute quantities of the conducting-powers and the laws according to which they depend on the content vary to a degree which is surprising in bodies which stand chemically so near one another.  $\text{CaCl}_2$  has a maximum (at 24 per cent.), and so has  $\text{MgCl}_2$  (at 20 per cent.). NaCl seems to go towards one; but it is questionable whether it reaches it before saturation (25.5 per cent.). The curve for  $\text{SrCl}_2$  is moderately curved; those for  $\text{BaCl}_2$  and  $\text{NH}_4\text{Cl}$  are less so; with  $\text{KCl}$  the conducting-power at  $18^\circ$  is almost exactly proportional to the salt-content. Indeed, from the Table for  $0^\circ$  it is seen that at this temperature the conducting-power of the  $\text{KCl}$  solution increases *somewhat faster than the percentage strength*, which has not, till now, been observed in any liquid.

As the above-mentioned minimum of the temperature-coefficient (see p. 421) and the maximum of conducting-power belong to the same liquids, the two properties appear to have an intimate connexion.

In general  $\text{BaCl}_2$  is the worst conductor; by far the best is  $\text{NH}_4\text{Cl}$ , which in a 25-per-cent. solution conducts about half as well as the best-conducting acids known, and, at all events, is the *best among all known salts*. It is to be presumed, since the solubility of  $\text{NH}_4\text{Cl}$  increases considerably with the temperature, that a solution saturated at  $100^\circ$  conducts at least as well as the best-conducting acid at the same temperature. Accordingly by

no means so high a place belongs to the acids as is generally assumed for them. In galvanic piles, for example, a nearly saturated solution of sal ammoniac can with advantage be employed in preference to the strongest acids that can be used for this purpose.

In another salt of ammonium, also, namely the nitrate, Wiedemann found a high conducting-power\*.

The behaviour of  $\text{MgCl}_2$  is remarkable. When the conducting-powers of its solutions are compared with those of the other chlorides of equal concentration, the former take the second place when very dilute, at 10 per cent. the fifth, and from 22 onward the last.

Nitric acid shows a maximum of conducting-power, namely for  $18^\circ$  when it contains 29.7 per cent.  $\text{HNO}_3$ . It was already found previously that a maximum belongs also to sulphuric and hydrochloric acids†. It appears remarkable that these *maximal conducting-powers of all three acids have nearly the same magnitude*. Attention has already been called to this by Quincke‡.

If we try to express the conducting-power  $k$  as a function of the salt-content  $p$ , we find that for the chlorides the form  $k = ap + bp^2 + cp^3$  renders the observations with tolerable completeness; but the conducting-power of nitric acid is not even approximately represented by this expression. As, moreover, empirical laws in which the number of terms is considerable present for calculation no advantage over a Table with an equidistant argument, nor exhibit in their coefficients a recognizable physical meaning, it would be superfluous to go further into this subject.

On the contrary, it is evidently important to compare quantitatively the different substances in those solutions in which they are at once comparable—that is, in but slight concentration. For the conducting-power of pure water is, in comparison with the above numbers, to be put sensibly equal to zero; and the course of the curves (p. 422) shows that the conducting-power constantly increases; consequently dilute solutions have a limit which the ratio of the conducting-power to the salt-content approaches: it may be named *the specific conducting-power of the substance in aqueous solution*. If the observations for the contents 0.05 and 0.1 (*i. e.* 5 and 10 per cent.) be expressed in the form

$$k = ap + bp^2,$$

$a$  will represent very nearly the specific conducting-power just

\* Pogg. Ann. vol. xcix. p. 228.

† Compare Pogg. Ann. vol. cxxxviii. p. 385, and vol. cli. p. 390.

‡ Pogg. Ann. vol. cxliv. p. 178.

now defined. At the same time it is immaterial for *a* whether the solution be reckoned in parts by weight (as is done here), or (as is more rational according to the definition of the conducting-power) by volume, since for dilute solutions the volume is equivalent to the weight. Also the quantity *b*, which denotes the initial deviation from proportionality, has a definite signification for each salt.

Only the results for 18° shall here be given, as their form for the other temperatures is very similar. They are:—

	<i>a.</i>	<i>b.</i>
NaCl . .	$k=0.000138p$	$-0.0000025p^2$
KCl . .	$k=0.000131p$	$-0.0000004p^2$
LiCl . .	$k=0.000160p$	$-0.0000046p^2$
NH <sub>4</sub> Cl . .	$k=0.000177p$	$-0.0000011p^2$
CaCl <sub>2</sub> . .	$k=0.000134p$	$-0.0000027p^2$
MgCl <sub>2</sub> . .	$k=0.000150p$	$-0.0000045p^2$
BaCl <sub>2</sub> . .	$k=0.000077p$	$-0.0000008p^2$
SrCl <sub>2</sub> . .	$k=0.000098p$	$-0.0000015p^2$
HNO <sub>3</sub> . .	$k=0.000534p$	$-0.0000101p^2$

According to this, the total character of each curve already shows itself while the content is yet very small: those substances which have a maximum of *k* at a definite degree of concentration, are distinguished by a relatively high value of *b*. (It may therefore be conjectured that LiCl also will show a maximum.)

If now we seek to connect the specific conducting-power *a* with other physical properties of the substances dissolved, we readily perceive that for the chlorides the quantities *a* stand nearly in the inverse order in a series to that of the equivalent-weights *A* of the anhydrous salts—indeed so that, *with equal amounts of chlorine in solution, the conducting-power of dilute solutions is not very different*. Still the deviations of the products *A . e* from their mean amount to as much as 22 per cent. (*Vide infra*.)

On the other hand, another accordance of an arrangement is self-evident—namely, according to the specific gravities *s* of the anhydrous salts. *The products s . a are, for the chlorides of the alkalies and alkaline earths, constant quantities, the greatest deviation from the mean being 12 per cent.* Although this deviation is not inconsiderable, yet so simple a relation is deserving of notice. If it were rigorously exact, it would signify that *equal volumes of anhydrous salts in solutions imply equal conducting-powers*.

In the following Table the salts are placed in the order of their conducting-powers *a*, and together with their equivalent-weights *A* and specific gravities *s*. For the latter I am indebted

partly to the memoirs\*, and partly to the information by letter, most kindly communicated, of H. Schröder.

A . a may be called the *specific conducting-power according to equivalents*; s . a that *according to volume*.

	a.	A.	A . a.	s.	s . a.
(NH <sub>4</sub> Cl) <sub>2</sub> ...	0.000177	107	0.0190	1.53	0.000271
(LiCl) <sub>2</sub> .....	160	85	136	2.04	326
MgCl <sub>2</sub> .....	150	95	142	1.89	283
(NaCl) <sub>2</sub> .....	138	117	162	2.16	298
CaCl <sub>2</sub> .....	134	111	148	2.20	295
(KCl) <sub>2</sub> .....	131	149	196	2.00	262
SrCl <sub>2</sub> .....	098	158	156	2.95	289
BaCl <sub>2</sub> .....	077	208	160	3.87	298

Finally, the quantity *b*, on which the amount of flexure of the curve depends (p. 422), appears in the case of the chlorides in general to stand in relation to the internal friction of the solutions, so far as ocular inspection can warrant a judgment on the latter property; for the liquids which have *b* large exhibit in general decidedly more viscosity with greater concentration than the rest†. On the other hand, nitric acid is still a very mobile liquid even when more concentrated, while it yet (as well as hydrochloric acid) has *b* large and exhibits again a diminution of conducting-power from a moderate percentage content onward.

It seems, then, that other molecular properties than the viscosity of solutions come into question here. At all events further data are requisite in order to accomplish a mechanical theory of electrolysis, perhaps upon the basis given by Quincke (*l. c.*).

Darmstadt, July 1874.

XLIX. *The Electrolysis of certain Metallic Chlorides.* By J. H. GLADSTONE, Ph.D., F.R.S., *Fullerian Professor of Chemistry in the Royal Institution*, and ALFRED TRIBE, F.C.S., *Lecturer on Chemistry in Dulwich College*‡.

WE have previously shown that nitrate of copper brought into tension by silver and copper in conjunction is decomposed by free oxygen in solution§. Thinking that chlorine might be substituted for oxygen, we commenced some experi-

\* Pogg. *Ann.* vol. cvi. p. 226, vol. cvii. p. 114, Suppl. vol. vi. p. 58; and a Monograph, 1873, Heidelberg.

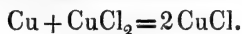
† Compare Hankel, Pogg. *Ann.* vol. lxi. p. 263; Wiedemann, *ibid.* vol. xcix. p. 229; and Beetz, *ibid.* vol. cxvii. p. 17.

‡ Read before the Physical Society, 1875. Communicated by the Society.

§ Proc. Roy. Soc. vol. xx. p. 290.

ments, employing chloride of copper, and observed some facts which seemed to have an interest from their bearing on the causation of galvanic action.

It is known that if metallic copper be placed in a solution of cupric chloride, it will slowly become covered with a crystalline deposit of the insoluble cuprous chloride:—



We found that when metallic copper and platinum are connected by a wire and immersed in cupric chloride, the insoluble salt forms not only upon the copper, but also on the platinum plate, as a white crystalline body. This deposit may generally be observed in about two minutes when the plates are three quarters of an inch apart. The formation of cuprous chloride upon the platinum plate takes place about equally rapidly in solutions containing 2·5 or 10 per cent. of salt. With a 20 per cent. solution the deposit was smaller, and with 40 per cent. practically *nil*, although there was abundant formation of cuprous chloride upon the *copper* plate.

We satisfied ourselves that the action took place equally well in solutions from which oxygen had been rigidly excluded, and also that a current passed from the copper to the platinum through the liquid—that is, from the metal of higher to that of lower potential.

In order to test whether this electrolysis of cupric chloride into  $\text{CuCl}$  and  $\text{Cl}$  could be effected by weak currents *ab extra*, we tried the effect of a zinc-platinum cell excited by common water and with platinum electrodes, and found that cuprous chloride deposited upon the negative electrode and chlorine at the positive, a little of which entered into combination with the platinum, but the greater part passed into the liquid. A cell excited with dilute sulphuric acid acted in a similar manner. A single Grove's cell gave for the first two or three minutes cuprous chloride on the negative platinum electrode, but afterwards metallic copper, while chlorine always formed at the positive plate.

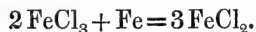
As zinc immersed in a salt of copper is capable of throwing down that metal, an experiment was tried with plates of zinc and platinum in connexion immersed in the chloride; the result was a more energetic action than with a copper-platinum couple similarly arranged, and besides a thick coat of cuprous chloride the edges of the platinum were incrustated with metallic copper. A similar magnesium-platinum couple gave a similar result, but with a decidedly greater proportion of metallic copper.

As there are two chlorides of mercury, similar to the two chlorides of copper, analogous experiments were tried with solution of corrosive sublimate.

A small bell-jar which terminated in a corked orifice was inverted and partly filled with mercury, over which was poured a solution of mercuric chloride; a wire passed from the mercury through the cork to a plate of platinum which hung in the solution, without, however, touching the mercury. On pouring the mercuric chloride upon the mercury, the metallic surface was at once dimmed by a film of mercurous chloride, which increased in quantity; and in the course of an hour or two the insoluble chloride appeared also on the platinum plate, and in twenty-four hours it was sufficiently thick to permit of its removal. On repeating this experiment with gold instead of platinum, the same mercurous chloride was deposited; but at the same time the gold plate was amalgamated, showing that the reduction of the mercuric chloride had not stopped at the first stage, but had actually proceeded to the separation of the metal itself. A similar gold plate immersed in the same solution of corrosive sublimate, but not in connexion with the mercury, showed no trace of deposit or amalgamation; and it was ascertained that gold alone has no power of decomposing moistened mercurous chloride.

An experiment was made with a current *ab extra*. A cell of Grove's was found to decompose mercuric chloride with the formation of the mercurous compound at the negative platinum electrode, while chlorine was given off at the positive one. This is in unison with what was found in the case of the copper salts.

That this action does not depend on the insolubility of the -ous chlorides was proved by the behaviour of the iron salts. Ordinary metallic iron is capable of reducing the ferric to the ferrous salt at the common temperature; thus:—



Platinum does not effect such a reduction; but when the iron is connected with platinum the change takes place more rapidly, and the reduced salt forms also on the negative metal. This, of course, does not render itself evident by any deposit, nor by any appreciable change of colour at first; but if the platinum plate be lifted out of the solution, and the liquid clinging to it be allowed to drain on to a paper moistened with some ferridcyanide of potassium, Turnbull's blue is the result. Or if a few drops of the ferridcyanide be mixed with the solution of the ferric chloride, on the junction of the iron and platinum the blue colour makes its appearance against each metal. Of course care was taken that the original salt contained no acid. The solution employed was one of 3·5 per cent. in strength.

If plates of magnesium and platinum be immersed in ferric chloride, metallic iron quickly makes its appearance on the platinum plate.

With a weak external battery and platinum electrodes the salt was resolved into chlorine and ferrous chloride, but with a strong battery into chlorine and iron—thus affording another instance of the close analogy between the primary electrolysis produced in the cell itself, and the secondary electrolysis that may be produced by an external battery.

L. *Researches in Acoustics*.

By ALFRED M. MAYER\*.—No. VII.

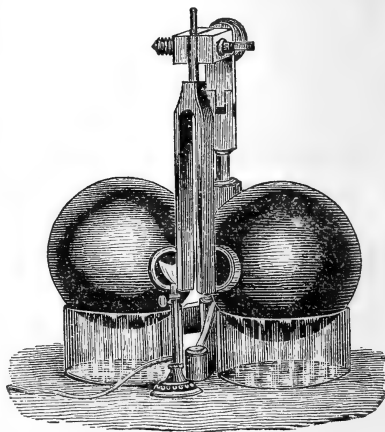
[Continued from p. 365.]

*Experiments on the Reflection of Sound from Flames and Heated Gases.*

THE reading of the recent interesting research of Professor Tyndall on "Experimental Demonstrations of the Stopping of Sound by partial Reflections in a non-homogeneous Atmosphere" (Proc. Roy. Soc. Jan. 1874; 'Nature,' Jan. 29, Feb. 5), and of the subsequent paper by Mr. Cottrell "On the Division of a Sound-Wave by a Layer of Flame or heated Gas into a reflected and a transmitted Wave" (Proc. Roy. Soc. Feb. 12, 1874), caused me to turn my attention to the experimental illustration of the reflection of sonorous vibrations from flames, heated gases, and from sheets of cold gases and vapours.

The following experiments are of easy execution, and show in a marked manner the reflecting-powers of sheets of flame and heated gas, and even serve to give approximate measures of these reflecting-powers.

Take two similar resonators and place the planes of their mouths at a right angle; then in this angle firmly fix the fork corresponding to the resonators, so that the broad face of one of its prongs faces the mouth of one resonator, while the space between the prongs faces the mouth of the other resonator. (See the figure.) By trial the two planes of the fork are placed at such distances from the resonators that



\* Communicated by the Author.



complete interference of the vibrations issuing from their mouths is obtained, and the only sound that reaches the ear is the faint sound given by the fork's action on the air outside the angle included by the mouths of the resonators. If in these circumstances we close the mouth of either resonator with a piece of cardboard, the open resonator will strongly reinforce the sound of the fork. If we now also cover the mouth of the latter resonator with a piece of cardboard we shall again have silence. Also, if we substitute, for one of the pieces of cardboard, a slip of stout glazed note-paper, the same result is obtained. But if we replace the piece of note-paper by a similar piece of French tracing-paper, a faint sound issues from the resonator so covered, because the tracing-paper is sufficiently permeable to sonorous vibrations to permit the resonator to slightly reinforce the sound of the fork. This reinforcement becomes greater if we substitute for the tracing-paper a piece of tissue paper, such as is used in printed books to cover steel engravings; and a yet greater reinforcement is produced when we put in the place of the tissue paper a piece of the soft, loosely woven paper which is used by French instrument-makers for the inner wrapping of their packed wares. I thus obtained a graded series of substances, more and more permeable to sonorous vibrations.

I again obtained neutralization by interference, with the mouths of the resonators open, and then screened the mouth of one of them with a bat's-wing coal-gas flame. The vibrations issuing from the resonators were now no longer neutralized, but the vibrations from the uncovered resonator had a great ascendancy over the other, so that a strong sound issued from it. I now tried to destroy this superiority by screening its mouth successively with the graded series of paper screens. The loose, soft paper was not equal to it; nor was the tissue paper; but the tracing-paper just equalled the effect of the gas-flame in guarding the mouth of the resonator from the entrance of sonorous vibrations. On lowering the gas-flame, so that its top luminous border was just below the mouth of the resonator, and therefore only a sheet of heated air ascended across the latter, the balance of the tissue paper against the hot gases and vapour remained unimpaired. Thus it appears that the reflecting-power of a sheet of coal-gas flame or of a sheet of the heated carbonic acid and vapour of water just above it, exactly equals, in the above described circumstances, the reflecting power of tracing-paper.

I have also found that the passage of a sheet of cold coal-gas across the mouth of the resonator was sufficient to destroy the balance of the interference, and caused a faint sound to issue from the other resonator; a similar effect, and nearly equal in

intensity, was obtained with a sheet of cold carbonic acid gas; while cold dry hydrogen closed the mouth of the resonator more effectively than either of the above gases, but was far inferior in this shielding action to the sheet of heated gases above the bat's-wing gas-flame. We should not place too much confidence in measures of the reflecting-power of surfaces made by the method just described, and which I have used merely to give approximations of the reflecting-powers of the above named gaseous sheets; for the substance which closes the mouth of the resonator may allow a considerable portion of the sonorous vibrations to enter the latter, and yet the resonator may not be able to reinforce the sound by reason of its being thus thrown out of tune with the fork by an unyielding surface closing its aperture. Thus, a sheet of thick note-paper prevents resonance as effectively as a thick piece of Bristol-board, or a plate of metal; yet we know well that these substances have very different powers to reflect sonorous vibrations. As a flat coal-gas flame equals a piece of tracing-paper in deflecting sonorous vibrations, it follows that we can substitute the former for the latter in all experiments where the presence of the paper produces, by its reflecting-power, an alteration in intensity or in pitch. Thus, if we vibrate a fork before the mouth of a resonator while the nipple of the latter is open, we obtain a far inferior reinforcement to what takes place when the nipple is closed. Now the nipple can be partly closed with a gas-flame or a sheet of heated air. Thus, alternately closing and opening the nipple of an  $Ut_4$  resonator with the flame of a Bunsen burner, gives excellent results\*. The reflecting-power of a bat's-wing flame is also well shown by successively closing and opening the mouth of any resonant box of forks in the octave  $Ut_4$  to  $Ut_5$ . Also, if the plug be taken out of the ends of closed organ-pipes and these pipes be placed horizontally, the reflecting effect of the flame is heard when the latter is passed forward and backward across the open ends of the pipes while the ear is placed in the axes of the pipes. The simplest method, however, is to sound the fork (either continuously by electro-magnetism, or by a bow) in front of its resonator, and successively to close and open the mouth of the latter with a flame or sheets of heated gas, or of cold vapours or gases. The contemplation of these experiments naturally calls up the question, Is the action of the flame due entirely to reflection? may it not also absorb part of the sonorous vibrations, as in the analogous phenomena of the reflection of light? If the intensity of the sonorous vibrations which have traversed the

\* In all of the experiments described in this paper care was taken that no heated air or gases entered the resonators and thereby put them out of tune.

flame equals the intensity of the vibrations which impinged on the flame minus the intensity of those which were reflected from the flame, then there is no absorption of these vibrations by the flame; but if this equality does not exist, then there is absorption in the flame; and this means that *the flame is heated by the sonorous vibrations*—which enter the flame as *sonorous vibrations*, but issue from the flame as *heat vibrations*. It thus, at first, appears that the absorption of the sonorous vibrations might be detected by their production of an increase in the temperature of the flame, just as sonorous vibrations are absorbed by caoutchouc and reappear as heat in this substance.

In the following manner I have recently made experiments in the direction of determining the equivalent of a given sonorous aerial vibration in fraction of a Joule's unit of 772 foot-pounds. I stretched between the prongs of an  $Ut_3$  tuning-fork a piece of sheet caoutchouc,  $\frac{1}{100}$  inch in thickness, and about  $\frac{1}{2}$  inch broad. The effect of this rubber on the vibrating fork is rapidly to extinguish its vibrations, while the rubber itself is heated; and if a fork be vibrated continuously by one and the same force when the rubber is stretched on it, and then when it is taken off, the aerial vibrations produced by the fork are far more intense in the latter circumstances than in the former. By a method described by me in Feb. 1871, I measured the relative intensities of the aerial vibrations in these two conditions of vibration. The sheet of caoutchouc was enclosed in a compound thermo-battery, and the fork vibrated during a known interval; the rubber was heated by the vibrations which would have appeared as sonorous vibrations if the rubber had been removed from the fork. The amount of heat given to the caoutchouc was accurately determined by the deflections of a Thomson reflecting-galvanometer connected with the thermo-battery; and by knowing the interval during which the fork vibrated, the amount of heat given to the caoutchouc during this interval, and the equivalent of the heated rubber in water, I calculated the intensity of the sonorous vibrations in terms of a thermal unit, from which I at once obtained the value of the sonorous aerial vibrations when the fork was not heating the rubber—in other words, when it vibrated freely. I thus found that the sonorous aerial vibrations produced during ten seconds by an  $Ut_3$  fork placed in front of its resonator, equalled about  $\frac{1}{100000}$  of a Joule's unit; that is, they can be expressed by the work done in lifting 54 grains one foot high. This quantity of heat, which is equal to the heating of one pound of water  $\frac{1}{100000}$  of a degree Fahr., expressed the amount by which the gas-flame would be heated if it absorbed all of the sonorous vibrations issuing from the  $Ut_3$  resonator. But this is such a small fraction of the

entire heat in the flame, that it is far within the actual fluctuations in its temperature; and even if the flame were constant in temperature, this small increase could not be detected by any known thermometric method. We cannot, therefore, determine the amount of absorptive power of a flame or of a sheet of heated air for sonorous vibrations by experiments on their increased temperatures when sonorous vibrations impinge on these bodies.

Hoboken, April 10th, 1874.

LI. *On some Phenomena connected with the Boiling of Liquids.*

By CHARLES TOMLINSON, F.R.S.\*

THE *Annales de Chimie et de Physique* for March 1875 contain a memoir by Professor Gernez, entitled "Recherches sur l'Ébullition." This memoir, which occupies sixty-six pages, has for its main object the support of De Luc's theory of ebullition, which "attributes the production of bubbles of vapour to the formation of bubbles of air." Upwards of one third of the memoir is devoted to historical notices, in which the author goes over nearly the same ground as that previously trodden by myself†. Several pages of the history are occupied with an account of my researches‡; and they are referred to again and again in other parts of the memoir. Of course I have no right to complain if M. Gernez, in the pursuit of a definite object, should refer to such of my experiments as suit his purpose, and pass over others which he either cannot or does not choose to assimilate with the theory he is advocating. He attaches great importance to the authorities that he quotes, and insinuates some surprise that I should venture to differ from them. That I did not ignore them is evident from the time and care bestowed by me in the compilation of my "Historical Notes," in which the results, as obtained by a large number of distinguished observers, were brought into juxtaposition for the first time. I did and do desire to treat those results with all the respect that is due to established facts; but I claim the right to form an independent judgment as to the inferences to be drawn from them. I gather from the memoir that M. Gernez does not quarrel with my facts, but only with their interpretation, although he seems to regard it as a fault in me that I do not consider the theory

\* Communicated by the Author.

† "Historical Notes on some Phenomena connected with the Boiling of Liquids," *Phil. Mag.* for March 1869.

‡ "On the Action of Solid Nuclei in liberating Vapour from Boiling Liquids," *Proceedings of the Royal Society*, 1869, vol. xvii. p. 240. An abstract of this paper appeared in *Les Mondes* of the 12th of October and 2nd of November, 1871.

of the distinguished Genevese sufficiently comprehensive to include all the phenomena, while he may regard it as a merit in himself to endeavour to confirm and support it. Nevertheless I beg to remind him that when the theory was started in 1772 it met with no favour, nor when it was restated in 1786; but when again brought forward in 1803 it was violently opposed in the very journal\* in which M. Gernez now advocates it. Nor was it until M. Donny published in 1846, in the same journal†, his remarkable researches that the theory rose at all into favour; but at that time, and even long after, the merit was given to Donny and not to De Luc. The details given in my "Historical Notes" established, I believe for the first time, the claim of De Luc, and the identity of Donny's results with his.

It is remarkable that although De Luc published his theory several times with very full experimental details, it attracted no attention, although many researches were being made about the same period, and the Committee of the Royal Society were considering their Report on Thermometers. De Luc was much in England and on intimate terms with many of the Fellows of the Royal Society, was admitted a Fellow himself in 1773, and as Reader to Queen Charlotte resided at Windsor and published several of his works, including the theory in question, in London. And yet his theory attracted no attention, and researches on the phenomena of boiling were made during upwards of half a century entirely without reference to this theory. Thus in 1784-85 Achard‡ studied the subject of boiling with reference to the material of the vessel and the influence of solid substances on the boiling-point. In 1812, and again in 1817, Gay-Lussac worked in the same direction as Achard, and also attached importance to the cohesion of the liquid, its adhesion to the sides of the vessel, as well as to pressure in influencing the boiling-point. In 1825 Bostock published his experiments on the boiling of ether and the influence of solids thereon; and still no reference is made to De Luc. Bostock suggests that the presence of air may have something to do with the results, but he has difficulty in explaining them on this ground. In 1835 Le Grand published some experiments on boiling, and endeavoured to show that the process becomes difficult in proportion as the air dissolved in the liquid is expelled. But I do not remember that he makes any reference to De Luc, any more than Magnus, who in 1836 recurred to the old idea of cohesion, or Schönbein,

\* *Ann. de Chim. et de Phys.* Ser. 1. vol. xlix. p. 235.

† *Ibid.* S. 3. vol. vi. p. 167.

‡ The references to the authorities here briefly enumerated are given in my "Historical Notes."

who in 1837 attributed the action of bits of wood, wire, &c. in liberating vapour from boiling liquids to the air contained in their pores or adhering to their surfaces, their action ceasing when the air is driven off. M. Gernez quotes this conclusion with applause; but he does not quote Schönbein's doubts, forgetting perhaps that the doubts of a man of genius are often of more value than the conclusions of an ordinary man. I pointed to the fact some years ago\* that Schönbein was by no means satisfied with the theory which attributed the action of solids in liberating gases or vapours from liquids to their carrying down air, a film of which was supposed to adhere to all bodies exposed to it; and he expressed his opinion that any one would perform an important service both to physics and to chemistry who could satisfactorily account for the varied phenomena connected with the subject of nuclei.

In 1842 Marcet attributed to differences of adhesion of the liquid to the sides of vessels of different material those differences in the boiling-point which had been so often noticed. In 1844 Magnus recurs to the same idea, and also to that of cohesion among the particles of the liquid; but they make no reference to the presence of gas in the liquid; and it was not until 1846, or three quarters of a century after the promulgation of De Luc's theory, that we have a De Luc *redivivus* in the person of M. Donny. According to him, boiling is not an inherent property of liquids; they only boil when they contain air—that is, when they are not pure. Heat liberates bubbles of air nearest to the source of heat; each air-bubble presents to the liquid molecules surrounding it a surface which promotes the vaporization of these molecules; and when the tension of the vapour is sufficient to counterbalance the pressure to which these bubbles are submitted, nothing further opposes the development of this vapour, which then forms currents that traverse the liquid and give rise to ebullition. Hence, according to this view, ebullition is a kind of evaporation; extremely rapid, which operates upon those interior surfaces of the liquid which limit a bubble of some æriform fluid. If the quantity of air in the liquid be small, the boiling-point may rise; the boiling-point is constant only when the liquid contains air. It is difficult, if not impossible, to get rid of the dissolved air. The boiling-point is also singularly influenced by the forces of cohesion and adhesion, the cohesion of the molecules of water being superior to a pressure of three atmospheres, or a column of water of 30 metres. This conclusion was arrived at by heating water in a chemically clean tube in a bath of chloride of calcium as high as  $138^{\circ}\text{C}$ . ( $280^{\circ}\text{F}$ .).

Donny's experiments excited considerable attention among

\* Phil. Mag. for September 1869.

physicists, but, so far as I know, did not have the effect of reviving De Luc's theory until I published an account of it in my "Historical Notes." From 1843 to 1863 it was considered a settled point that, in proportion as water is deprived of air, the character of its ebullition changes, becoming, as it does, more and more abrupt, and boiling, like sulphuric acid, with frequent *soubresauts*, and the water becomes superheated until relieved by a burst of vapour. In 1863 Mr. Grove stated that if water be boiled in an open vessel it continually reabsorbs air and boils in the ordinary way—although, in a tube with a narrow orifice and with a layer of oil on the water, however long the boiling be continued, a minute bead of nitrogen gas is always to be detected. I have already made some remarks on this form of experiment\*. About the same time the experiments of M. Dufour excited considerable attention. In order to get rid of the adhesion of the liquid to the sides of the vessel, he heated a mixture of oil of cloves and linseed-oil and dropped into it water heated to  $80^{\circ}$  or  $90^{\circ}$  C., and then gradually raised the temperature of the bath, in one case until it reached  $178^{\circ}$  C. ( $352^{\circ} \cdot 4$  F.); and he supposed the water to be at that high temperature without boiling. Many years ago I showed that drops of water, ether, alcohol, &c. could be deposited on oil heated to  $450^{\circ}$  or  $500^{\circ}$  F. when they assumed the spheroidal state and rolled about on the surface for a long time: In some cases when a drop slipped beneath the surface it exploded and scattered the oil about; but in other cases it was shot up again to the surface, where it continued to roll about as before. Hence I ventured to suggest in my "Historical Notes" that the globules in Dufour's experiment were in the spheroidal state, especially as he admits that when they touched the side of the vessel or were touched with solids introduced into the bath they exploded. But what strengthens my suspicion is the admission on the part of M. Dufour that globules of water, although still retaining their dissolved air, admit of being superheated in his oil-bath. This is exactly what I found in my experiments on the spheroidal condition of liquids on hot oil; the globules that sank without exploding contained air, but were protected from the superior heat of the oil by a coating of vapour and by slow vaporization from the surface.

As to the action of solid nuclei, M. Dufour admits that his results were not always concordant, but were even sometimes contradictory; and he attributes these irregularities to differences in the surface of bodies, to greater or less degrees of roughness, to the absence or presence of foreign corpuscles adhering to them, to the presence or absence of an adhering film of air;

\* Phil. Mag. for March 1872.

and he attributes the sudden change of state in the globules from liquid to vapour to the capillary action of porous bodies.

The various effects obtained by me from solid nuclei in what I term the chemically unclean or non-catharized state, are admitted by M. Gernez (p. 356); but, while refusing to admit my explanation of them, he invokes the aid of M. Verdet (p. 352), who says:—"The following cause acts doubtless in many cases, perhaps in all. If in certain parts [of the solids] the surface be not wetted by the liquid, and if in these parts there exist very small and very fine asperities, the capillary forces compel the liquid to withdraw from the sides to the neighbourhood of these asperities (as happens when we dip a very fine steel needle into mercury); and in this way is formed a veritable free surface where evaporation is a constant and necessary phenomenon. When the vapour formed between this free surface and the side has acquired a sufficient elastic force, it becomes disengaged and ebullition sets in. In this way it may be explained how sulphur and shellac, which water does not wet, and metals which it wets less completely than glass, are useful in accelerating ebullition. In M. Donny's experiment it was necessary that the tube be first disembarassed from fatty matter by washing with sulphuric acid; the prolonged boiling of the water had probably for its final object, not only the getting rid of the dissolved air, but also the bringing about a certain chemical action of the water on the glass, the result of which was to produce a more intimate contact and a stronger adhesion."

All this is put forth with great ingenuity and ability. At the risk of being tedious, I must here repeat my theoretical views as to the function of solid surfaces introduced into a gaseous solution, or into a liquid at or near the boiling-point. The term "gaseous supersaturated solution" refers to such liquids as soda-water, Seltzer water, champagne, &c.; and seeing that, in a large number of cases in which solid nuclei separated gas from them, there was a precisely similar action of nuclei in separating vapour from liquids at or near the boiling-point, it seemed not unreasonable to suppose that these last-named liquids are constituted like the former. (Herr Schröder subsequently adopted the same view\*.) Moreover in both cases the received opinion is that nuclei act by carrying down air, into which the gas or the vapour is said to expand, and so escape; whereas, according to my theory, I endeavour to show that as gas or vapour will adhere to an oily, fatty, or greasy body, or to a body that has been handled, while water will not so adhere, it is only necessary to introduce such a body into the solution to see that it becomes

\* Poggendorff's *Annalen*, 1869.



immediately covered with bubbles of gas or of vapour. These bubbles escape from its surface so long as it continues to be covered, more or less, with a film of a body that can be touched by gas or vapour and not by water. A flint pebble that has been exposed to the air of a room or handled and put into a solution of gas or of vapour, immediately becomes covered with bubbles; but if broken in half and returned to the solution, not a single bubble is to be seen on the fractured parts; for these are specimens of nature's clean surfaces\*. If air has any action to perform in the matter, why should the unclean and not the clean surfaces carry it down?

Some liquids contain their own nuclei, as in the case of milk. When this is heated over the fire it becomes more and more charged with vapour; and at a certain point the particles of butter disseminated through it, assisting the expansive force of the heat, produce such a sudden burst of vapour as to cause the liquid to boil over.

If a body, such as a glass rod, be made chemically clean and then be plunged into a supersaturated solution of gas or of vapour, not a single bubble will be seen upon it, because the solution, whether of water and gas, or water and vapour, adheres to it perfectly. If the clean but wet glass rod be left to dry in the dusty air of the room, and when dry be plunged into the solution, it will be active; but if left to dry in the pure outer air of the country, and when dry be plunged into the solution, it is inactive, because it is still in a clean or catharized state.

But it is contended by M. Gernez, and before him by Herr Schröder, that the effect of washing the glass rod or other solid surface in sulphuric acid, or in a caustic alkaline solution, is to get rid of the film of air that adheres to it; while Herr Schröder admits that unclean bodies act because they are covered more or less with a film of fatty organic matter, but according to him it is this film which enables the air to adhere to the solid. This is the critical point of the inquiry. I say that when a clean glass rod or wire &c. is drawn through the hand and immediately immersed in a supersaturated solution, the gas or the vapour is in a condition to leave the solution and adhere to the unclean surface. If an unclean glass rod be heated and introduced below the surface of the solution, and by moving it against the clean side of the vessel leave a greasy line, such line becomes instantly covered with gas- or vapour-bubbles. A rod or wire heated in the flame of a spirit-lamp not sufficient to clean it,

\* M. Gernez broke a Prince Rupert's drop below the surface of a super-heated liquid; the fragments did not act because, according to him, they contained no air. I say they were inactive because they were chemically clean.

but sufficient to burn off any air, if air existed, still acts as a nucleus.

In my paper in the 'Proceedings' the following experiment is given :—

"It is said that rough bodies are most favourable to the liberation of vapour. The hot carbonic disulphide was touched with a rat's-tail file, and it produced furious boiling. The file was then held in the flame of a spirit-lamp, and while hot placed in the upper part of the tube, so that it might cool down to about the temperature of the liquid and yet be sheltered from the air. On touching the surface of the disulphide with the end of the file, there was no liberation of vapour; and the file was slowly passed to the bottom of the liquid, but still there was no action. The file was now taken out and waved in the air; on reinserting it into the liquid, there was a burst of vapour, arising from some mote or speck of dust caught by the file from the air. The file was quickly cleaned by the liquid, and it became inactive as before. It was again taken out and waved in the air; and on once more putting it into the liquid, boiling set in again."

But, according to M. Gernez, the file instead of catching nuclear particles caught air, which it reintroduced into the hot liquid. He does not attempt to explain the following experiment, although he refers to the paper containing it\*.

Wood-spirit, boiling at  $140^{\circ}$  F., contained in a test-tube, was plunged into a flask of hot water. A clean glass rod that had been exposed during an hour to the air of my garden was inactive. It was drawn through the hand that had been made slightly greasy with lard, and when reinserted it produced such a burst of vapour as to turn out half the contents of the tube.

A similar result was produced with ether and bisulphide of carbon.

Surely I am not exceeding the bounds of philosophical discretion in insisting that a theory of boiling that does not include within its generalizing influence such results as the above must be defective.

I have endeavoured to show† that solids, in their action on gaseous or vaporous solutions, admit of being arranged into four classes :—(1) Vitreous bodies and certain metals which, in a catharized or chemically clean state, have no nuclear action, because there is perfect adhesion between them and the solution. (2) Bodies that are not wetted by the water of the solution, but to which the gas or vapour can adhere. Such are fatty or oleaginous bodies and also resinous bodies; these act as nuclei.

\* "Reply to the Rev. Father Solaro in *Les Mondes*, Dec. 21, 1871," *Phil. Mag.* March 1872.

† *Phil. Mag.* April 1873.

(3) Porous bodies, such as charcoal, coke, the various woods, meerschaum, chalk, &c.; these act as permanent nuclei. (4) Soluble substances, such as sugar, gamboge, &c., which act as nuclei by diminishing adhesion between the gas or vapour and the water. A body in Class 1 is said to be chemically unclean when it is contaminated by a body in Class 2.

M. Gernez regards these bodies merely as vehicles for conveying air into the body of the liquid; he maintains that such bodies have no nuclear action *per se*, that porous bodies, such as charcoal, and resinous and fatty bodies, such as shellac, stearine, &c., have no specific action, because when deprived of air by repeated boiling they become inactive. I have not been able to deprive fragments of cocoa-nut-shell charcoal of their nuclear character, although employed in distillations for days and weeks together. My first paper contains some numerical results showing how singularly efficacious cocoa-nut-shell charcoal is in separating vapour from boiling liquids and increasing the amount of the distillate; and on this account the use of porous nuclei in such operations is strongly recommended. M. Gernez also, in his practical applications at the end of his memoir, gives similar advice.

I felt the point in dispute to be of such importance that I repeated the directions of M. Gernez, namely to boil what I call a permanent nucleus a number of times at short intervals. For this purpose I selected a fragment of cocoa-nut-shell charcoal. Mr. Hunter has taught us\* how powerfully and rapidly this substance absorbs vapours at various high temperatures—such as 255·4 times its volume of the vapour of a mixture of 10 cubic centims. of absolute alcohol and 30 cubic centims. of water, 150 times its volume of methylic alcohol, 261·8 of a mixture of 10 cubic centims. of methylic alcohol and 20 cubic centims. of water, 117 of bisulphide of carbon, 87 of ether, 116 of acetic ether. These measurements were all taken at 100° C. The mean of several observations for vapour of water gave 43·9 volumes absorbed at 127° C. Accordingly water was boiled over the flame of a spirit-lamp in a clean tube in the presence of a triangular fragment of cocoa-nut-shell charcoal. It was boiled eleven times, at intervals of rather more than five minutes, as M. Gernez directs. While the tube was still warm it was put under the receiver of an air-pump; and the exhaustion had not proceeded far when a violent burst of vapour from the charcoal turned out about one third of the water from the tube. The tube was again boiled, plugged with cotton-wool, and left for about three hours. It was again placed under the receiver, and

\* Journal of the Chemical Society, vol. iii. 1865, p. 215. See also vols. v, & vi.

the exhaustion was made as perfect as possible. Not a single bubble was visible either by daylight or by candlelight. Had there been a bubble in any part of the tube it must have been detected, since the bubbles have the lustre of mercury. On again holding the tube over the flame, the charcoal gave a few crackling sounds and then emitted vapour in abundance, and the boiling was as easy as at first. Next morning abundance of air-bubbles were given off during the boiling, showing that air had been absorbed during the night.

I do not see any *à priori* reason why the charcoal, as a nucleus, should be exhausted. Its absorptive powers remain, whether for vapour or gas, whatever number of times the same specimen be used. In Mr. Hunter's experiments the air was expelled by raising the charcoal to a red heat and quenching it under mercury before introducing it into the vapour. When used as a nucleus in boiling, the air is gradually displaced by the vapour; it is continually absorbing vapour and emitting it under the continued action of the heat. Its action resembles those catalytic processes in which a body remaining apparently unchanged brings about continuous changes in another body—as, for example, where the presence of a small quantity of black oxide of manganese enables chlorate of potash to liberate its oxygen at a moderate heat. There is probably a continuous formation of permanganic acid at the expense of the chlorate, and a continuous decomposition under the continued action of the heat, the function of the oxide being to transfer oxygen from the state of combination to the free state. So also the charcoal, by its strong absorptive power, transfers vapour from the liquid, but cannot retain it at the high temperature, so that there is a continual absorption and a continual emission. When after repeated boilings the liquid is left to cool, a moderate heat is sufficient to start the charcoal as a nucleus; and if left during twelve or fourteen hours, air is absorbed, and the action is then the same as with a fresh piece of charcoal.

I give one or two more examples of permanent nuclei. A bit of gutta percha was boiled with water in a clean tube; it softened under the heat; and a glass rod was introduced so as to press it against the side of the tube near the bottom and leave a smear, while the greater portion was removed adhering to the rod. This smear was singularly active in liberating bubbles of vapour; and after the lamp was removed, bubbles were dragged upwards from it so as to become pear-shaped. The tube was boiled eight times, at intervals of from 5 to 20 minutes; but the smear continued to maintain its activity. Next morning the tube was boiled again, and the smear was active as before.

The inside of a tube was extensively smeared with lead soap.

The boiling was singularly vigorous, every part of the smear originating rapidly ascending bubbles of vapour, which boiled over.

Such experiments as these may be multiplied to any extent. Their results seem to me to be eloquent in favour of the action of nuclei in liberating vapour. Such action may be explained by M. Verdet's theory, or by that of M. Gernez, or by my own. I say they are active because the vapour adheres to them and the water does not; but I think it can hardly be maintained that their action is due to air, seeing that in the course of these repeated boilings air is expelled while the nuclei continue as active as ever, and it is only after twelve hours or so of repose that air is reabsorbed in any appreciable quantity.

The following cases of nuclear action are taken from a paper read by me before the Society of Arts on the 7th of April, 1869, entitled "On the Theory of Boiling in connexion with some Processes in the Useful Arts."

1. In some of the old colliery engines of Scotland, when the steam becomes slack and there is no time for cleaning out the boiler, the engine-men are accustomed to throw into it about a bushel of the radicles of barley, produced during the malting and separated in cleaning the malt. The effect of these radicles (or *comings* as the men call them) becomes immediately apparent on again raising the steam; for not only is there an abundant supply for producing the full working-speed of the engine, but an excess going to waste at the safety-valve. This singular effect will continue during several days\*.

2. In the distillation of ardent spirits on a large scale it is customary, when converting the wash into what are called "low wines," to throw a lump of soap into the still every time it is charged. This has the effect not only of causing the steam to rise more quietly, but the vapour is more free from the residual matter of the process.

3. The sugar-boilers are accustomed to throw a lump of butter into the vacuum-pan for the purpose of preventing that irregular boiling which displays itself in furious bursts, separated by apparently almost passive intervals. Solid paraffin is now preferred to butter in producing regular boiling.

4. Professor Oersted† noticed that if a metallic wire be suspended in a boiling liquid, it instantly becomes covered with bubbles of vapour. To show the application of this fact, 10 lbs. of brass wire,  $\frac{1}{8}$  of a line in diameter, were put into a still containing ten pints of brandy; seven pints came over at a heat which, in the absence of the wire, would have sent over only four.

\* Edinburgh Philosophical Journal, O. S. vol. ii. p. 340.

† Gehlen's Journal, vol. i. p. 277.

5. It is well known in the laboratory that in distilling ether, alcohol, and similar liquids in glass vessels, the vapour is given off with difficulty. At one moment the liquid does not boil at all, at another it bursts into a mass of vapour and liquid which fills the vessel and occasions such a bumping of the retort as to endanger its safety, and, indeed, sometimes to break it. The vapour forms, in fact, with a sort of dull explosion which is very marked in distilling sulphuric acid. These bumpings are called *soubresauts* by the French. They are mitigated if not prevented by introducing into the retort some solid matter not acted upon by the liquid. It is recommended to use sharp, or angular, or rough pieces of metal, glass &c., the points being, it is supposed, favourable to the generation of steam. Silver, platinum, or copper (in the form of foil or wire or filings), or bits of cork or cartridge paper are recommended by Dr. Faraday as "promoters of vaporization"\*.

It seems to me in such cases as the above that the various substances act by the adhesion to them of the vapour and its consequent separation under the continued action of the heat, and that they cease to act as soon as they become chemically clean, in which case the vaporous solution adheres to them as a whole†.

Throughout his memoir M. Gernez avoids the use of the term chemically clean, and attributes the varied behaviour of solid nuclei simply and solely to the adhering air. Air and air only is the means by which bubbles of vapour can escape from a liquid at or above the boiling-point; and for this purpose the minutest speck is all-sufficient. Get rid of this speck of air, and boiling becomes impossible; the liquid becomes more and more superheated, and then suddenly goes off with an explosion. But to get rid of this speck of air is the difficulty. It persists in remaining; and so efficacious is it that, although it may not be more than a millimetre in diameter, it will continue its action during twenty-four hours and liberate upwards of half a million of bubbles of vapour, each bubble about five millimetres in diameter. However marvellous this result may appear, the proposition at the head of the subdivision 3° on the next page (p. 380) is still more so, namely that "each bubble of vapour is formed at the

\* Chemical Manipulation, 1830, p. 199.

† A friend, writing from the laboratory of a manufacture (May 6, 1875), says:—"We have had some difficulty in determining our boiling-points. We were very careful at first in cleaning our tubes and thermometers; and the result was that we did not get water to boil under 216° or 217° F. Now, after cleaning all the parts thoroughly, we rub the thermometer-stem and bulb with a duster in use in the laboratory, and get the boiling-points all right." I recommended him to put a bit of cocoa-nut-shell charcoal into the liquid.

expense of a certain quantity of air." M. Gernez says:—"Each bubble of vapour produced during the ebullition draws off with it a certain quantity of air. This proposition is contrary to the opinion of Mr. Tomlinson, who regards it as improbable. Nevertheless it may be seen *à priori*, from the very nature (*disposition*) of the experiment, that the initial bubble of air occupying the whole cavity of the bell [that is, a minute bell-glass full of air attached to a glass rod and lowered into the water] expands with the vapour formed at the surface of the liquid, so that it is a bubble of mixed air and vapour that escapes. Whatever number of bubbles be disengaged, there will always remain a determinate fraction, although infinitely small, of the quantity of air that existed at the commencement."

That is, every one of the half million of bubbles that escapes draws upon the bubble of air of which the initial diameter is one millimetre; and, however long the process be continued, this rapidly diminishing speck of air never vanishes altogether, but continues to maintain the ebullition to infinity.

Even if the small bell be filled with water instead of air, and by a brisk application of the flame the water be made to boil, the little bell becomes filled with steam, and this carries on the operation for an indefinite time; but we are told that if the water be left to cool, a minute speck of air will be found in the bell.

Of course with such ideas as these M. Gernez objects to my definition of a liquid at or near the boiling-point, namely that it is a supersaturated solution of its own vapour, on the ground that it implies that in the same point of space there are at the same temperature the same substance in the liquid state and in the state of vapour. A liquid supersaturated with its own vapour is as easy to conceive as a liquid supersaturated with a gas; and since the behaviour of the various nuclei is the same in both, I infer that they are constituted alike. A fatty, or resinous, or porous body to which the water will not adhere, but the gas or the vapour will, is an efficient nucleus in separating gas or vapour from solution, provided the one or the other already exists in the liquid; while there is no such separating action if the solid be of vitreous structure and chemically clean. M. Gernez admits that carbonic acid gas, ammoniacal gas, &c. do exist in their gaseous solutions; but he cannot admit that the vapour of water, for example, exists in solution when the water is raised to the boiling-point or superheated. What, then, is the definition of such a liquid? According to M. Gernez, it is "a supersaturated solution of the gases of the air." Now, in the case of recently distilled water we may dismiss carbonic acid. If the water be cold, it is capable of dissolving only one fiftieth

of its volume of nitrogen and one twenty-fifth of its volume of oxygen; and these small quantities must be reduced to an almost inappreciable amount in hot or boiling water. But M. Gernez assumes that in raising water to the boiling-point very little of the dissolved air is expelled by the heat, that so much of it remains as to convert the liquid into a supersaturated solution of oxygen and nitrogen; that is, the water contains more of these gases at any given high temperature up to boiling or superheating than it could absorb at such temperatures; and he justifies his assertion by the statement that, however long the water be allowed to boil, a speck of air can always be detected in it, as already noticed. And he quotes an experiment by M. F. Marco, the description of which is entitled "*Démonstration de la cause mécanique de l'ébullition.*" He says, "I take a thermometer-tube with a spherical bulb at its extremity and break the bulb so that there remains a tube with a sort of funnel with irregular edges. I plunge this tube into water contained in a matrass, so that the funnel rests on the bottom of the matrass. I have thus a small mass of air imprisoned by the funnel and by the water. I afterwards heat the water to boiling by means of the flame of a spirit-lamp. Then, by a suitable arrangement of the flame, bubbles of vapour may be seen to escape continually from the funnel." M. Gernez, who claims the priority in this experiment, remarks that it shows in an interesting manner the part played by air in the ebullition of liquids. At the same time I may remark that, supposing such to be the case, it does not exclude other modes of liberating vapour, although, according to M. Gernez, access of air is the only mode.

I have repeated this experiment with a small thermometer-tube and a thin cylindrical bulb, the end of which had been broken off. Now, what is the action of this small bell-glass, lowered, full of air, to the bottom of a tube 8 inches in length,  $1\frac{1}{2}$  inch in diameter, containing a depth of 6 inches of water? The first effect is to compress the air and to admit a portion of water into the bell. When heat is applied the air expands, expels the water, and a portion of the air escapes in the form of a bubble. A larger quantity of water now enters the bell; and as the heat slowly increases, the remaining volume of air again expands, forces out the water, and another bubble escapes; more water enters; but the water is now charged with vapour which rises into the bell and mingles with the small amount of air that remains in it. Expansion goes on as before; another bubble of mixed air and vapour escapes; water charged with vapour again ascends, but is forced back by another bubble of vapour and a still smaller proportion of air; and in this way a sort of oscillatory motion is kept up, until most of the air is got



rid of and bubbles of nearly pure vapour escape. The vapour rises into the bell just as gas does into a jar of water at the pneumatic trough, and would remain but for the heated bottom of the flask near to the source of heat, which is hotter than any other part of the arrangement. This superior heat causes the vapour in the little bell constantly to expand and discharge itself; but it does not do so continuously, it is an oscillation between vapour escaping and vapour charged with water entering—an oscillatory motion which, as I have said, is only possible at the bottom of the vessel (at least in this form of the experiment), where the heat is most intense. If the little bell be raised some way above the heated bottom it ceases to act, no vapour escapes; and hence I say that this experiment does not show that air has the exclusive function assigned to it. The heated bottom of the vessel is the chief source of the bubbles of steam. They may be seen flashing from this hot surface, rising upwards and rapidly vanishing if the liquid has not yet attained its boiling-point, or bursting on the surface when that point has been attained. There are also certain specks in the bottom of glass flasks, retorts, tubes, &c. which act as powerful nuclei; they discharge streams of bubbles with unceasing vigour, which does not decline although the action be continued during many hours. At the same time I do not deny, never have denied, that the air in solution has a useful part to perform in lessening the forces of cohesion and adhesion in the liquid, and in facilitating the formation of bubbles of vapour. All I contend for is that air is not the only nucleus, but that there are other modes of separating gas or vapour from their solutions, as already pointed out.

I am quite prepared to admit that, seeing how vast a number of important vital functions depend on the solubility of air in water, a portion of air should cling obstinately to water even when raised to high temperatures, or, by virtue of this property, even when expelled by boiling, air may be, as Mr. Grove suggested, continually reabsorbed at or near the boiling temperature; and I should prefer to adopt this view rather than the idea that a bubble of air one millim. in diameter is an efficient cause in liberating half a million of bubbles of steam, each five millims. in diameter.

I arranged M. Marco's experiment on a larger scale by employing a short tube nearly 2 inches in length and about  $\frac{3}{8}$  inch in diameter. A few coils of thin binding wire were passed round it near the bottom and also near the mouth of the tube; each coil terminated in a loop; and to each loop was attached, also by a loop, a longer and stouter wire extending beyond the neck of the flask. In this way, without removing the tube from the

flask, it could be easily arranged with the mouth downwards or upwards. A globular flask containing above ten ounces of distilled water was employed. When the mouth of the small tube was downwards the phenomena were much the same as before, only the tube did not rest on the bottom unless held there. On removing the lamp, the tube rapidly filled and sank with its mouth upon the heated bottom, which expanding the enclosed vapour caused it to disgorge the water and so to rise again. It did this two or three times; it then settled and filled; but there remained a small bead of air about the size of the head of a small pin. On again applying the lamp, the water boiled readily; but 75 seconds elapsed before the tube became active; and it was not until bubbles of vapour passed up into it and displaced the water that the tube was in a condition to pour out its intermittent bubbles; and it seems to me of importance to insist on this point, namely that on this as on many other occasions the flask boiled, so to speak, from its own independent resources, long before the little bell or the small tube came into action at all; and when either of them did so it behaved simply as a nucleus, increasing the amount of vapour that was given off by the boiling liquid. The flask boiled first from the action of the heated bottom and the presence of minute specks, probably of carbon, on the surface of the bottom, the importance of which I insisted on in my first paper. The air in the bell or in the small tube was displaced by expansion; and if at length the whole of the air was not got rid of, the reason seems to be the impossibility of doing so by expansion, just as it is impossible to obtain a perfect vacuum in the receiver of an ordinary air-pump. The air in the receiver goes on expanding until an exceedingly thin medium is left; and the air in the tube in boiling water is pumped out by expansion, and the minute portion that at length remains shows, not that this speck is necessary to carry on the ebullition, but simply that it is impossible to exhaust the tube by expansion only. Hence I see no reason to qualify the statement made in my first paper, namely that I cannot help thinking that too much importance has been attached to this small residual speck of air in the phenomena of boiling liquids. If a speck of air be thus left in the tube, a minute portion also probably exists in other parts of the liquid, although I have failed to detect it. Moreover by repeatedly boiling the flask at intervals of five or ten minutes, and allowing the small tube to fill after each boiling, the water becomes so far purged of air that the speck in the tube disappears, or is so minute that I have been unable to pronounce as to its existence. Of course it may have entered into solution even during the observation.

In some of the low-boiling liquids the speck rapidly dimi-

nishes and disappears. For example, in distilling wood-spirit (boiling-point  $148^{\circ}$  F.), a small tube, held by a thin wire passing through the cork, stood with its mouth near the bottom of the retort. After the fifth boiling, when the lamp had been removed, the tube poured out about 150 bubbles of vapour before it began to fill. It occupied three minutes in filling, and then a minute speck was visible by the aid of a lens; but within another minute the liquid closed over this speck and it disappeared, the temperature of the liquid being as high as  $128^{\circ}$  F. M. Gernez would say that the speck had entered into solution, after which the boiling would become difficult. On the contrary, the boiling was just as easy as before.

M. Gernez is so impressed with the necessity for the intervention of air in the phenomena we have been considering, that he cannot do without it in accounting for the line of bubbles which is produced by the friction of a chemically clean solid against the inner side of a chemically clean vessel containing a supersaturated gaseous solution or a liquid at or near the boiling-point. I have already endeavoured to give a simple explanation of these phenomena\*. "The glass rod or the steel knitting-needle, on being pressed against the side of the glass, displaces a certain small quantity of the liquid, and on moving the solid, with friction, against the side, successive quantities of liquid are thus displaced. A certain time, however short, must elapse before the water can fairly close in upon the moving points of the line thus traced; but however quick the water may be in filling up the void, the gas is quicker, and hence a friction line becomes a line of bubbles."

M. Gernez says:—"As it results from these divers experiments that in each bubble of vapour disengaged there is always a small quantity of air, it is natural to suppose that the friction of solid bodies in the middle of a liquid should determine the separation of a small quantity of gas which was in a state of supersaturated solution and which serves as an atmosphere into which the liquid emits vapour."

Considering how minute a portion of air or gas liquids at or near the boiling-point, and especially after repeated boiling, can hold in solution—considering also that such liquids when removed from the source of heat, can be made to boil up again and even to boil over, by the mere friction of a hard solid, I cannot conceive that these multitudes of bubbles are called into existence by first liberating air; but I can conceive that the vapour, being already in solution in the hot liquid, is in a condition to rush into the vacuum formed for it by a solid moving against the side.

\* *Phil. Mag.* for November 1874.

There are some other points arising out of the long memoir of M. Gernez, especially on the subject of superheating, that call for comment, but must be deferred to another occasion on account of the great length of this paper.

Highgate, N. May 10, 1875.

LII. *Remarks on M. Goldstein's Observations on Spectra of Gases.* By Professor WÜLLNER, of Aachen\*.

IN the *Monatsbericht* of the Königl. Akademie der Wissenschaften for August last are described by M. Goldstein observations on gas-spectra †, which are said to prove that my explanation of the band- and line-spectra observed in one and the same gas (*Pogg. Ann.* vol. cxlvii. p. 321) is untenable. My explanation was to this effect—that from an illuminating gas a band-spectrum is always obtained when a thick layer of gas is made use of as the source of light, but the line-spectrum when only a few molecules of the gas are ignited. I deduce this from experiments which showed that in tubes filled with rarefied gases the line-spectrum always and only appeared when the induction-current traversed the tube in the form of a proper spark, but the band-spectrum when the discharge was without a spark. In my experiments at that time the sparkless discharge was that which I afterwards (*Pogg. Ann.* Jubelband) named the luminous tuft: it gives light which more or less fills the entire tube; the proper spark ignites a minimum quantity of molecules, only those which lie in the line of the spark.

The experiments of M. Goldstein which are said to contradict my explanation consist, so far as I understand his description, essentially in this:—In the circuit in which is the spectral tube he produces an interruption at one place, so that there the induction-current passes in sparks; sometimes he also inserts a Leyden jar; and then he observes the spectra of the tube. He expects under these circumstances line-spectra must appear in the tube, but finds, as a rule, in tubes filled with air, the band-spectrum, and only when the air presents greater resistance a mixed spectrum of bands and lines. No detailed description is given of his observations on hydrogen; he merely remarks (p. 602), “The observations on hydrogen correspond.” He specifies, however, that, of two tubes simultaneously placed in the circuit, one containing air, and the other hydrogen, the former gives the band-spectrum, and the latter the line-spectrum. As the same

\*. Translated from the *Monatsbericht der Königlich Preussischen Akademie der Wissenschaften zu Berlin*, December 1874.

† See *Phil. Mag.* for May 1875, pp. 333–345.

rhythm of the discharge was present in every part of the circuit, M. Goldstein believes that when at one place there is a spark it also appears at all places in the circuit at which interruption takes place, that consequently, according to my explanation of spectra, the line-spectrum would everywhere show itself.

I see, on the contrary, in the experiments of M. Goldstein in general a corroboration of my view, which requires a band-spectrum whenever extensive masses of gas are rendered luminous. The error in M. Goldstein's assumptions is this:—When at one place in the circuit the discharge passes in a spark, he infers that it must also do so in all spectral tubes inserted, because the rhythm of the discharge is everywhere the same. This is not the case; the form in which the discharge takes place in spectral tubes depends on the pressure of the gas and on the dimensions of the tube.

That like rhythm does not establish like form, I have already shown in my treatise on the origin of spectra of different orders (*Pogg. Ann.* vol. cxlvii. p. 337), where, in one and the same hydrogen-tube, the spark extended only from the positive electrode about halfway down the tube, but below this it was dissolved. If the slit of the spectrometer was on a level with the spark, it gave the line-spectrum; if it was in front of that part of the tube in which the spark was lost, the band-spectrum was seen.

M. Goldstein himself has also observed that in spaces containing air sufficiently rarefied, in spite of the insertion of a spark-distance, no spark comes, when he (in p. 603 of his communication) speaks of several centimetres thickness. He even alternated sparks with a discharge as rapid as the spark. That (as M. Goldstein truly remarks) such a discharge does not give a line-spectrum, is the best proof of the correctness of my interpretation of the phenomena; for in that case the whole of the light filling the tube shines, and not, as in proper sparks, merely a few molecules lying in the line of the spark.

Last year I made a great number of experiments on the passage of the induction-current through tubes filled with rarefied gases; and in those experiments, exactly as M. Goldstein did, I interposed spark-distances, and sometimes also Leyden jars. I have not been able to finish those experiments, because working at the new edition of my *Experimentalphysik* has claimed the whole of my attention. I have on this account communicated only a small portion of them, treating of the forms of the positive luminous tuft, in tubes filled with air, in its dependence on pressure and on the dimensions of the tube. Let me be permitted here to communicate a series of experiments from March 1873, carried out in conjunction with Dr. Winkel-

mann, which, as it seems to me, pretty well elucidate the phenomena in question.

The tube used for these experiments had a uniform diameter of 2 centims., the points of the electrodes being 8 centims. distant from each other. Besides the tube, a Riess spark-micrometer was placed in the circuit, by which such spark-distances as I pleased could be inserted. The method of conducting the observations was that which I had previously employed, and is described in Pogg. *Ann.* vol. cxlvii.

If the exhaustion of the tube was a minimum, with a long spark-distance the discharge passed only in the same rhythm as in the spark, but it filled the entire tube; the spectrum is not the line-spectrum, but the band-spectrum not sharply shaded. If the spark-distance be diminished, there follows upon the first momentary discharge a positive luminous tuft showing stratification (that described in the Jubelband of Poggendorff's *Annalen*). The number of strata increases as the spark-distance decreases; when the distance is short, but still just sufficient to exclude the closing-current, four strata are visible.

At about 1 millim. pressure, if a spark-distance of 30 millims. be inserted, the discharge commences with a momentary partial discharge which fills the tube, followed immediately by a positive luminous tuft with stratification. The spectrum is the band-spectrum. With decreasing spark-distance the stratification becomes sharper, and in the spectrum the shadings appear more distinct.

With an air-pressure of 4 millims. and without a spark-distance the positive tuft, completely filling half of the tube, appears as a perfectly continuous field of light; but when a spark-distance is inserted, first the momentarily passing bluish discharge shows itself, and the positive tuft takes the form of a cloud (described by P. A. in the Jubelband). Band-spectrum.

Pressure 25 millims. A small spark-distance gives at the commencement a partial discharge, visible in the rotating mirror as an unspread image of the tube; then follows a luminous tuft at the positive electrode in the form of two clouds. If the spark-distance is taken very great, only the momentary partial discharges appear, which fill the tube each time with whitish blue light. In the spectrum the shadings are no longer distinctly recognizable; but not a line of the line-spectrum is to be seen.

Pressure 45 millims. Without a spark-distance the light divides in the rotating mirror into four clouds. With a spark-distance of 30 millims. the clouds have nearly vanished, and the current passes only in 3-4 discharges, which in the rotating mirror give unspread images of the tube; but the spectrum is still the band-spectrum, only not so sharply shaded. On

shortening the spark-distance the clouds gradually develop ; and when it is reduced to 20 millims. they are already completely formed, but are of shorter duration than when there is no spark-distance. With 65 millims. pressure the number of clouds rises to five or six ; in other respects the appearance is substantially as before.

Pressure 100 millims. Without a spark-distance, essentially a positive luminous tuft, in the shape of a great number of clouds, which give the band-spectrum. When a spark-distance of 10 millims. is interpolated, there appears a small and feeble spark, in the rotating mirror as a fine line of white light opening the discharge ; but it reaches only about 1 centim. below the positive electrode, and is there lost in the diffused discharge, as before described in the case of hydrogen. On increasing the spark-distance inserted, the spark extends further ; with one of 30 millims. it sometimes goes quite over from one electrode to the other. *When the spark enters, the green lines of the line-spectrum immediately appear in the band-spectrum otherwise furnished by the tube, and exactly as far as the spark extends ; so that in the spectrum the length of the spark can be accurately ascertained, even without the aid of the rotating mirror.*

Pressure 145 millims. Without the interpolation of a spark-distance the current passes at first in the form of a partial discharge ; then follows a positive tuft which appears in the rotating mirror as flickering clouds. The insertion of a spark-distance of 12 millims. sometimes produces in the tube a very peculiar spark-discharge : from the positive electrode springs a spark to about the distance of 1 centim. in the tube, and is there lost, but reappears 1 centim. lower down, looking again like a spark-line 1 centim. in length. Sometimes the spark is present as a line along this whole distance ; but it never goes further than about half the distance between the two electrodes. Only with the external interpolation of a greater spark-distance does the spark in the tube become longer ; and when the former amounts to 30 millims. the latter sometimes extends the whole distance from one electrode to the other. The spectrum of the spark shows, besides the green, even the yellow and red lines of the nitrogen line-spectrum. *The lines, however, are to be seen in the spectrum only just as far as the spark extends (here, as before, I copy, word for word, the note made at the time) ; hence we can recognize in the spectrum precisely to what distance the spark reaches.*

The above-related series of experiments consequently shows unequivocally that a spark-distance interpolated in the circuit of the induction-current by no means always calls forth sparks in spaces filled with rarefied gases, even with uniform rhythm of the

discharge, but that the occurrence of sparks depends much more on the pressure of the enclosed gas and on the length of the interpolated spark-distance. As long as, in the space filled with rarefied air, the discharge does not pass in a proper spark, only the band-spectrum appears; when the spark enters, the lines of the line-spectrum also are seen.

With respect to the formation of the spark and with it the appearance of the line-spectrum under circumstances otherwise the same, viz. equal pressure and equal spark-distance, I have as yet not been able to verify in air any perceptible influence of the dimensions of the tube in which the air is enclosed; according to M. Goldstein's observations, such an influence seems to be present, just as I have observed it in hydrogen. In reference to this, I take leave to quote a sentence or two from the forth-coming new edition of the 2nd volume of my *Experimentalphysik*, because it at the same time explains the fact that, of two tubes simultaneously inserted in the circuit, with a capillary intervening portion, the one tube containing air, and the other hydrogen, the former shows the band-spectrum, the other the line-spectrum.

After giving the explanation deduced by me from the observations on wide tubes, I say (p. 252):—"The same difference in the thickness of the luminous layer is also present in tubes with an intervening capillary piece, as appears from the course of the phenomena being the same in my experiments on the nitrogen-spectrum (Pogg. *Ann.* vol. cxxxvii.); there also the thickness of the layer of gas which fills the capillary tube is still very great in comparison with the fine line of the proper spark. That some gases, rendered incandescent by the induction-current, give only the line-spectrum depends on this, that the current can only pass through them in sparks. It is worthy of note that in narrow tubes, even with hydrogen, in slight pressures the spark-discharge appears together with the sparkless one; in a tube of 1 centim. diameter I almost constantly saw the spark-discharge; and in tubes with a capillary between them, in slight pressures the spark-discharge often came alone, without that luminous tuft. This circumstance accounts for the fact that, in Geissler tubes with a capillary between-piece, we often obtain only the line-spectrum, and often the same accompanied by the band-spectrum."

Hereby, probably, the most important of M. Goldstein's objections are answered. With respect to the thick sparks giving the line-spectrum (p. 340), I only add that, leaving out of view the fact that it is very difficult to give a definite judgment on the thickness of a spark, every spark (if we designate as such an entire discharge apparently taking place in one spark) consists of a great number of partial discharges following one another in



very rapid succession. On this account we cannot expect the band-spectrum even with apparently very thick sparks, as, even when the quantity of electricity passing in the spark was rising, I constantly obtained only the unshaded continuous spectrum in addition to the line-spectrum or developed out of it.

After the foregoing, it is unnecessary at present to go into M. Goldstein's further experiments, some of them very interesting; closer consideration shows that not one of them contains any contradiction of my explanation of spectra. I reserve to myself a more detailed examination of them when I have opportunity to finish and communicate the above-mentioned experiments on the forms of the discharges in spaces filled with rarefied gases.

LIII. *On the Flow of Electricity in a uniform plane conducting Surface.*—Part I. By G. CAREY FOSTER, F.R.S., and OLIVER J. LODGE.

[Concluded from p. 400.]

[With a Plate.]

22. **RESISTANCE.**—The resistance, in the direction of the flow, of the part of the sheet extending between two given equipotential circles follows directly from equation (4) (in § 19). Thus for the potentials of the circles characterized by the ratios  $r_1 : r'_1$  and  $r_2 : r'_2$  respectively, where  $r_1$  and  $r_2$  are distances from the source, and  $r'_1$  and  $r'_2$  the corresponding distances from the sink, we have

$$U_1 = \frac{Q}{2\pi\kappa\delta} \log \frac{r'_1}{r_1} \quad \text{and} \quad U_2 = \frac{Q}{2\pi\kappa\delta} \log \frac{r'_2}{r_2},$$

whence

$$U_1 - U_2 = \frac{Q}{2\pi\kappa\delta} \log \frac{r'_1 r_2}{r_1 r'_2}.$$

Consequently the resistance of the part of the sheet between these circles is

$$R = \frac{U_1 - U_2}{Q} = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{r'_1 r_2}{r_1 r'_2} \quad \dots \quad (5)$$

If  $\rho_1$  is the radius of the circle which has the greater absolute potential, or the one nearest the source, and  $\rho_2$  is the radius of the circle nearest the sink, the similarity of the triangles APC and BPC in fig. 2, Plate IX., gives

$$\frac{\rho_1}{a + d_1} = \frac{r_1}{r'_1} \quad \text{and} \quad \frac{\rho_2}{a + d_2} = \frac{r_2}{r'_2}$$

for circles round the source, and

$$\frac{\rho_1}{a+d_1} = \frac{r'_1}{r'} \text{ and } \frac{\rho_2}{a+d_2} = \frac{r'_2}{r'}$$

for circles round the sink. Substituting these values, we get

$$R' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{\rho_2(a+d_1)}{\rho_1(a+d_2)}$$

if both circles surround the source, and

$$R' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{\rho_1(a+d_2)}{\rho_2(a+d_1)}$$

if they both surround the sink. In the former case we have  $\rho_1 < \rho_2$ , and in the latter case  $\rho_1 > \rho_2$ ; but using  $\rho_1$  for the radius of the smaller circle and  $\rho_2$  for that of the larger, we may write

$$R' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{\rho_2(a+d_1)}{\rho_1(a+d_2)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

for the resistance between two equipotential circles surrounding the same pole, whether that pole be a source or a sink.

If the circles surround opposite poles, the resistance becomes

$$R'' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{(a+d_1)(a+d_2)}{\rho_1\rho_2} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In the case of circles round the same pole, if the other pole is infinitely distant, the value of  $R'$  becomes

$$\frac{1}{2\pi\kappa\delta} \log \frac{\rho_2}{\rho_1},$$

which is identical with (1), the value found for the resistance of an annular belt of internal radius  $\rho_1$  and external radius  $\rho_2$ ; and in fact the case supposed (an infinite distance between source and sink) is physically identical with the case of a single pole in an infinite sheet.

When the circles surround opposite poles, if the radii are equal, the resistance becomes

$$\frac{1}{\pi\kappa\delta} \log \frac{a+d}{\rho} \text{ or } \frac{1}{\pi\kappa\delta} \log \frac{a+\sqrt{a^2+\rho^2}}{\rho};$$

or when the common radius is small as compared with  $a$ ,

$$R = \frac{1}{\pi\kappa\delta} \log \frac{2a}{\rho} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

23. The following modified forms of (6) and (7) obtained by means of the relations (§ 20)

$$\frac{a+d}{\rho} = \frac{\rho}{h}, \quad a^2 = ll', \quad 2\rho = l-l',$$

may also be noted :

$$\left. \begin{aligned} R' &= \frac{1}{2\pi\kappa\delta} \log \frac{\rho_1 h_2}{\rho_2 h_1}, \\ R'' &= \frac{1}{2\pi\kappa\delta} \log \frac{\rho_1 \rho_2}{h_1 h_2}, \end{aligned} \right\} \quad (9)$$

$$\left. \begin{aligned} R' &= \frac{1}{2\pi\kappa\delta} \log \frac{(\sqrt{l'_1} - \sqrt{l_1})(\sqrt{l'_2} + \sqrt{l_2})}{(\sqrt{l'_1} + \sqrt{l_1})(\sqrt{l'_2} - \sqrt{l_2})}, \\ R'' &= \frac{1}{2\pi\kappa\delta} \log \frac{(\sqrt{l'_1} + \sqrt{l_1})(\sqrt{l'_2} + \sqrt{l_2})}{(\sqrt{l'_1} - \sqrt{l_1})(\sqrt{l'_2} - \sqrt{l_2})}. \end{aligned} \right\} \quad (10)$$

24. If two equipotential circles alone are given and it is required to find the resistance between them, the position of the poles A and B being unknown, the expressions given above for  $R'$  and  $R''$  are inapplicable (unless the circles are so small that their centres sensibly coincide with the poles); for in such cases the values of  $r$ ,  $r'$ ,  $a$ ,  $d$ ,  $h$ , and  $l$  are all unknown. The distance, however, between the centres of the circles is directly measurable; and the resistance can be expressed in terms of this distance and of the known radii as follows.

Calling the distance between the centres  $D$ , we have for circles surrounding the same pole,

$$D = d_2 - d_1 = \sqrt{a^2 + \rho_2^2} - \sqrt{a^2 + \rho_1^2},$$

which gives

$$d_1 = \sqrt{a^2 + \rho_1^2} = \frac{\rho_1^2 - \rho_2^2 - D^2}{2D}, \quad d_2 = \sqrt{a^2 + \rho_2^2} = \frac{\rho_1^2 - \rho_2^2 + D^2}{2D},$$

and

$$a = \frac{\sqrt{(\rho_1 + \rho_2 + D)(\rho_1 + \rho_2 - D)(\rho_1 - \rho_2 + D)(\rho_1 - \rho_2 - D)}}{2D}.$$

Hence (6) may be written \*

$$R' = \frac{1}{2\pi\kappa\delta} \log$$

$$\frac{\rho_2 \sqrt{(\rho_1 + \rho_2 + D)(\rho_1 + \rho_2 - D)(\rho_1 - \rho_2 + D)(\rho_1 - \rho_2 - D)} + \rho_1^2 - \rho_2^2 - D^2}{\rho_1 \sqrt{(\rho_1 + \rho_2 + D)(\rho_1 + \rho_2 - D)(\rho_1 - \rho_2 + D)(\rho_1 - \rho_2 - D)} + \rho_1^2 - \rho_2^2 + D^2}. \quad (11)$$

When the equipotential circles surround different poles, we have

$$D = d_1 + d_2 = \sqrt{a^2 + \rho_1^2} + \sqrt{a^2 + \rho_2^2},$$

\* This expression was given in a slightly different form by Gauguin on the authority of Blavier (*Ann. de Chim. et de Phys.* Ser. 3. vol. lxvi. p. 203. 1862); and a demonstration has since been published by the latter (*Journal de Physique*, vol. iii. p. 115, April 1874).

which gives

$$d_1 = \sqrt{a^2 + \rho_1^2} = \frac{D^2 + (\rho_1^2 - \rho_2^2)}{2D}, \quad d_2 = \sqrt{a^2 + \rho_2^2} = \frac{D^2 - (\rho_1^2 - \rho_2^2)}{2D},$$

and  $a$  the same as before. Hence (7) may be written

$$R'' = \frac{1}{2\pi\kappa\delta} \log$$

$$\frac{\sqrt{(\rho_1 + \rho_2 + D)(\rho_1 + \rho_2 - D)(\rho_1 - \rho_2 + D)(\rho_1 - \rho_2 - D) - \rho_1^2 - \rho_2^2 + D^2}}{2\rho_1\rho_2}. \quad (12)$$

25. If instead of considering the whole extent of the sheet we confine our attention to that part of it which is contained between any two lines of flow (see Plate IX.), its resistance will be given by any of the above formulæ if instead of  $2\pi$  in the denominator we put the angle, say  $\gamma$ , which the lines of flow forming the boundaries make with each other at either pole; for the spaces between every pair of consecutive flow-lines convey equal currents; and since the difference of potential between their ends is the same for all, they all have the same resistance. Consequently the resistance of a part of the sheet made up of such spaces is inversely proportional to the number of them which compose it. Now, using as previously  $\alpha$  to stand for the angle which two consecutive lines of flow make with each other at the poles, the total number of spaces into which the whole sheet is divided is  $\frac{2\pi}{\alpha}$ , and the number of spaces lying between lines of

flow whose angle at the poles is  $\gamma$ , is  $\frac{\gamma}{\alpha}$ ; hence, if  $R_\gamma$  is the resistance of the part of the sheet bounded by these lines, and  $R$  the resistance of the whole of the sheet, we have

$$\frac{R_\gamma}{R} = \frac{2\pi}{\gamma}.$$

In the case of two flow-lines which form arcs of the same circle drawn through the two poles, we have  $\gamma = \pi$ , and therefore

$$R_\gamma = 2R.$$

Hence, if a small equipotential circle is drawn round each pole, the resistance of the part of the sheet lying between these circles and contained within any circle drawn through the poles is the same, being equal to twice the resistance of the unlimited sheet between the same two equipotential circles, and also equal to the resistance of as much of the unlimited sheet as would be left after cutting out the portion bounded by any circle through the poles. Consequently if  $\rho$  is the common radius of the small

equipotential circles, we have, for the resistance of a disk on the edges of which the poles are situated, and also for that of the space outside it, according to §§ 22 & 24,

$$R = \frac{2}{\pi\kappa\delta} \cdot \log \frac{2a}{\rho} \quad \text{or} \quad R = \frac{2}{\pi\kappa\delta} \cdot \log \frac{D}{\rho}. \quad . \quad . \quad (13)$$

26. It may be observed that the method by which the resistance was obtained above (§ 22) is essentially the same as that adopted by Kirchhoff. The method by which we first obtained the expression, however, was founded on the consideration of the equality of the resistance of the curvilinear rectangles into which the sheet is divided by the intersecting systems of lines of flow and equipotential lines (*vide* Plate IX.). This process, which may be stated as follows, we afterwards found to be somewhat similar in principle to that employed by Smaasen.

Let two circular electrodes be placed upon the sheet so as to coincide with two of the natural equipotential circles, which for simplicity we will assume to have the same radius ( $=\rho$ ). The spaces between consecutive lines of flow are of equal resistance, and may for the present purpose be regarded as so many independent conductors connecting the two poles and combined in multiple arc. Consequently the resistance of the sheet which is made up of these spaces, is equal to the resistance of one of them divided by their whole number. These spaces in their turn are each composed of  $2n$  equi-resisting rectangles arranged in series; so the resistance of each space is  $2n$  times the resistance of one of the rectangles,  $2n$  being (as is evident from Plate IX.) the whole number of equipotential lines in the sheet which are not obliterated by the electrodes.

Now consider the resistance of one of the four rectangles at the middle of the figure. Its length  $OD = l = a \frac{\mu-1}{\mu+1}$  (§ 20) (for,  $n=0$  giving the straight equipotential line through  $O$  (§ 19), the next one will be given by  $n=1$ ). Its breadth  $b$ , which in fig. 3 is denoted by  $CQ$ , will be

$$a \cot \frac{\pi-\alpha}{2} = a \tan \frac{\alpha}{2}.$$

Calling  $\delta$  the thickness and  $\kappa$  the conductivity of the sheet as before; the resistance of the rectangle will be approximately

$$R_0 = \frac{l}{b\kappa\delta} = \frac{1}{\kappa\delta \tan \frac{1}{2}\alpha} \cdot \frac{\mu-1}{\mu+1}.$$

The number of equipotential lines between the electrodes is  $2n$  if the electrodes are of equal size and coincide with the  $n$ th

equipotential circle on each side of the middle line. The radius of this circle is given in § 20 as

$$\rho = \frac{2a\mu^n}{\mu^{2n}-1};$$

solving which we get

$$\mu^n = \frac{a \pm \sqrt{a^2 + \rho^2}}{\rho}.$$

The positive sign only is admissible, since  $\mu$  is essentially positive; whence the number of lines

$$2n = \frac{2}{\log \mu} \log \frac{a + \sqrt{a^2 + \rho^2}}{\rho}.$$

So, then, the resistance of a strip between two consecutive flow-lines is

$$R_1 = 2nR_0 = \frac{2}{(\mu+1)\kappa\delta \tan \frac{1}{2}\alpha} \cdot \frac{\mu-1}{\log \mu} \log \frac{a + \sqrt{a^2 + \rho^2}}{\rho}.$$

The number of flow-lines in the sheet is (§ 12)

$$\frac{2\pi}{\alpha};$$

therefore the resistance of the whole sheet is approximately

$$R = \frac{\alpha}{2\pi} R_1 = \frac{1}{(\mu+1)\pi\kappa\delta} \cdot \frac{\alpha}{\tan \frac{1}{2}\alpha} \cdot \frac{\mu-1}{\log \mu} \log \frac{a + \sqrt{a^2 + \rho^2}}{\rho}.$$

Now, make the rectangles infinitely small (and therefore rectangular), by letting  $\alpha$  approach 0 and  $\mu$  approach 1; then

$$R = \frac{1}{\pi\kappa\delta} \log \frac{a + \sqrt{a^2 + \rho^2}}{\rho},$$

the same expression as that obtained at the end of § 22 for the same case.

The resistance of the segment contained between two flow-lines intersecting each other with the angle  $\gamma$  is, under the same circumstances (§ 25),

$$R_\gamma = \frac{2}{\gamma\kappa\delta} \log \frac{a + \sqrt{a^2 + \rho^2}}{\rho} \dots \dots \dots (14)$$

#### *Any number of Poles in an Infinite Sheet.*

27. *Lines of Flow.*—The equation to the flow-lines for two equal and opposite poles, A and B, in an unlimited sheet, was

obtained in § 11 in the following form,

$$\angle APB = n\alpha,$$

where  $n$  is a parameter whose value changes by unity on passing from one line to the next, and  $\alpha$  is the angle between adjacent rays of the equiangular pencil of flow-lines produced by either pole separately. If the straight line AB be taken as the axis of  $x$ , the above equation may be written

$$\angle APB = \angle PBX - \angle PAX = n\alpha.$$

Moreover it was shown, in § 10, that the system of flow-lines resulting from the composition of any two similar systems is obtained by drawing lines through the alternate angles of the quadrilaterals produced by the mutual intersection of the lines of the component systems, in directions concurrent with both the flow-lines which intersect each other at each angle. Hence, if the poles A and B (Pl. IX. fig. 1) were of the same sign (both sources or both sinks), the lines of flow of the resultant system, instead of passing through the points P, Q, R and P<sub>1</sub>, Q<sub>1</sub>, R<sub>1</sub>, &c., as there represented, would pass through the supplementary angles of the quadrilaterals, namely from Q' to P<sub>1</sub>, from R' to Q<sub>1</sub>, &c. It is evident that, as we pass from point to point of a line so drawn, the angles which the *radii vectores* from the poles make with the axis of  $x$  change equally, but in opposite directions; hence this equation may be written

$$\angle PBX + \angle PAX = n\alpha.$$

28. If, instead of the line through the poles, any other straight line in the plane of flow be taken as the direction of reference for measuring the angles made by the *radii vectores*, the form in which the equations to the lines of flow have just been given will still be applicable. Thus, if the line X (Pl. X. fig. 1), making any angle  $\delta$  with A B, be taken as the direction of reference, and if  $a$  and  $b$  be the points where it is met by P A and P B respectively, it is clear that the angles P  $a$  X and P  $b$  X are each of them less than the previous angles P A X and P B X by the angle  $\delta$ , but that for each flow-line they give a constant sum or difference according as the poles are of the same or of opposite kinds. Hence, denoting the angles which the *radii vectores* make with any fixed line by  $\theta_1$  and  $\theta_2$  respectively, and agreeing to distinguish sources and sinks by a difference of intrinsic sign of the angles corresponding to them, we may write the equation to the flow-lines due to two equal poles, whether similar or opposite, in the general form

$$\theta_1 + \theta_2 = n\alpha.$$

29. In like manner, the lines of flow due to any number of

equal poles are represented by the equation  $\Sigma\theta = n\alpha$ , the angles which the *radii vectores* from the several poles make with any fixed line being respectively denoted by  $\theta_1, \theta_2, \dots$ . In order to prove this, it is sufficient to show that, if the expression holds good for any given number of poles, it will still be true for one pole more; for since the formula has been proved for two poles, this would enable us to advance, by successive additions of one pole at a time, to any number.

Let, then, the curves  $P''Q'R$ ,  $P'QR_1$ , and  $PQR_2$  (Pl. X. fig. 2) represent parts of three successive lines of flow due to any number  $k$  of equal poles, and let them be characterized respectively by the following values of  $\Sigma\theta$ , namely  $(n+1)\alpha$ ,  $n\alpha$ , and  $(n-1)\alpha$ . If there is another pole of the same strength at  $L$ , which we will suppose in the first instance to be a *source*, the pencil of flow-lines diverging from it with the common difference of angle  $\alpha$  will intersect the flow-lines from the  $k$  sources, producing a number of quadrilaterals through whose opposite angles the lines of flow will pass which result from the action of the pole at  $L$  combined with that of all the rest (§ 10). If the direction of the flow along the lines of the component systems be as represented by the arrow-heads\* in the figure, one line of the resultant system will pass through the points  $P'$  and  $Q'$ , another through  $P$ ,  $Q$ , and  $R$ , and a third through  $Q_1$  and  $R_1$ . Let the lines joining the source  $L$  with the points  $P$ ,  $Q$ , and  $R$  cut the fixed line  $X$  in  $p$ ,  $q$ , and  $r$  respectively; then, for the flow-line through  $Q$  due to the  $k$  poles, we have by hypothesis

$$\theta_1 + \theta_2 + \dots + \theta_k = n\alpha;$$

and for the line through the same point due to the source  $L$  we have

$$\angle QqX = m\alpha,$$

and therefore, for both together,

$$\Sigma\theta + QqX = (n+m)\alpha;$$

For the point  $P$ , we have similarly

$$\Sigma\theta + PpX = (n-1)\alpha + (m+1)\alpha;$$

\* For the purpose of the argument in the text, we may assume arbitrarily either the *direction of flow* along the assumed system of lines of flow, or the *direction of increase* in the value of  $n$  (in  $n\alpha$ ), but not both; for a definite assumption regarding one of these conditions determines the other also. If the system of flow-lines for any given set of poles is built up by successive repetitions for one pole at a time of the construction given in § 10, it will be found that the conventional distinction between positive and negative angles leads to the following rule as to the connexion between the two above-named conditions:—Going along a given flow-line *with the flow*, any line on the *left hand* corresponds to a *higher* value of  $n$  than the given line, while a line on the *right hand* corresponds to a *lower* value of  $n$ .



and for the point R we have

$$\Sigma\theta + RrX = (n+1)\alpha + (m-1)\alpha.$$

Consequently for each of these points, which we already know are situated on the same flow-line of the resultant system, we have

$$\theta_1 + \theta_2 + \dots + \theta_k + \theta_l = (n+m)\alpha.$$

In the same way, we should get for the points P' and Q' situated on the line of flow of the resultant system which lies next to the line through P, Q, and R on the left, the respective values which follow :

$$\Sigma\theta + P'pX = n\alpha + (m+1)\alpha,$$

$$\Sigma\theta + Q'qX = (n+1)\alpha + m\alpha,$$

and therefore for each of them

$$\theta_1 + \dots + \theta_k + \theta_l = (n+m+1)\alpha.$$

The same reasoning gives for the points Q<sub>1</sub> and R<sub>1</sub> on the line of flow next on the right to that through P, Q, and R,

$$\theta_1 + \dots + \theta_k + \theta_l = (n+m-1)\alpha.$$

30. Next suppose the additional pole at L to be a *sink*; then, since the resultant flow must be everywhere concurrent with both the components, the new flow-lines will pass through the other pair of angles of each quadrilateral; for instance, three consecutive lines will pass through the points P' and Q<sub>1</sub>, through P'', Q, and R<sub>2</sub>, and through Q' and R<sub>1</sub>; and by applying the same considerations as above, it will be seen that these lines are characterized by the following values of the expression

$$\theta_1 + \dots + \theta_k + \theta_l,$$

namely :—for the line through P' and Q<sub>1</sub>,

$$(n-m+1)\alpha;$$

for that through P'', Q, and R<sub>2</sub>,

$$(n-m)\alpha;$$

and for that through Q' and R<sub>1</sub>,

$$(n-m-1)\alpha.$$

Hence it follows that sources and sinks affect the value of the sum of angles denoted by  $\Sigma\theta$  in opposite ways, and therefore that, as assumed provisionally above (§ 28), sources and sinks must be distinguished by a difference in the intrinsic sign of the angles which the *radii vectores* drawn from them make with the fixed line. When this is done, the equation

$$\Sigma\theta = n\alpha$$

is true for the lines of flow produced by any number of equal poles, whether of the same sign or not.

Further, if we have poles of unequal strengths supplying (or removing) quantities of electricity in the unit of time denoted, say, by  $Q_1, Q_2, \dots$ , these may be regarded as each of them produced by the coalescence of a corresponding number of equal poles supplying in unit of time a quantity of electricity  $q$  which is taken small enough to be a common measure of all the quantities  $Q_1, Q_2, \dots$ . In applying the general formula to such a case, the value of  $\theta$  corresponding to each pole would have to be taken a number of times equal to the number of constituent poles of strength  $q$  required to make up the actual pole. Hence

$$\Sigma(Q\theta) = Q_1\theta_1 + Q_2\theta_2 + \dots = na \quad \dots \quad (15)$$

is a perfectly general expression for the lines of flow produced by any number of poles of any strength.

31. *Equipotential Lines*.—It was shown in § 17 that the system of equipotential lines resulting from the composition of any two systems, for which the constant difference of potential on passing from one line to another is the same, is given by drawing lines through the alternate angles of the quadrilaterals formed by the mutual intersection of the lines of the component systems, if the angles are taken in such order that on going from any one to the next we pass, in one of the component systems, to a line of higher, and in the other to one of lower potential. We know also (see § 5) that the equipotential lines due to a single pole are concentric circles whose radii vary according to the terms of a geometrical progression, the potential increasing in the case of a source as the radii decrease, and, in the case of a sink, as the radii increase. Hence it follows very simply, by the application of reasoning exactly analogous to that employed in § 29, that if  $P$  be a point on an equipotential line due to any number of equal sources at the points  $A, B, C, \dots$ , and sinks at the points  $A', B', \dots$ ,

$$\frac{AP \cdot BP \cdot CP \dots}{A'P \cdot B'P \dots} = \mu^n = \text{constant},$$

where  $\mu$  is the constant ratio of the radii of consecutive equipotential circles due to a single pole, while  $n$  is a number characteristic of the particular line on which the point  $P$  is situated and increasing by unity if this point passes from any given line to the line of next lower potential. For shortness we may put  $r_1$  for  $AP$ ,  $r_2$  for  $BP, \dots$ , and write the above equation thus,

$$\frac{r_1 \cdot r_2 \cdot r_3 \dots}{r'_1 \cdot r'_2 \dots} = \mu^n,$$

or

$$\Sigma \log r = n \log \mu.$$

32. No part of the above reasoning will be disturbed if we suppose that each of the equal poles hitherto discussed emits (or absorbs) in unit of time a quantity of electricity equal to unity; and as this supposition will simplify the consideration of poles of unequal strength, we will adopt it. Then, when the poles are unequal, let them severally emit in unit of time quantities of electricity represented respectively by  $Q_1, Q_2, Q_3, \dots$  (the absorption of electricity by sinks being reckoned as negative emission), the effect will be the same as if  $Q_1, Q_2, \dots$  poles of unit strength coincided at the points occupied by the actual poles. Hence, in such a case, the *radii vectores* from the several poles must be taken  $Q_1, Q_2, \dots$  times in the above formula, and it thus becomes

$$\left. \begin{aligned} & r_1^{Q_1} \cdot r_2^{Q_2} \cdot r_3^{Q_3} \dots = \mu^n \\ & \Sigma (Q \log r) = n \log \mu, \end{aligned} \right\} \dots \dots (16)$$

which is a quite general expression for the equipotential lines due to any distribution of poles of any strength.

33. To find the actual potential at any point due to a given set of poles, we must recur to equation (2), § 7. Let  $V_1, V_2, \dots$  be the potentials which the various poles would produce at the given point if each acted separately, and let  $\phi_1, \phi_2, \dots$  be the potentials produced by each separately at unit distance from itself; then, taking the other symbols in the senses already defined, we have

$$\begin{aligned} V_1 &= \phi_1 - \frac{Q_1}{2\pi\kappa\delta} \cdot \log r_1, \\ V_2 &= \phi_2 - \frac{Q_2}{2\pi\kappa\delta} \cdot \log r_2; \\ &\vdots \end{aligned}$$

and for the resultant potential at the given point,

$$U = \Sigma V = \Sigma \phi - \frac{1}{2\pi\kappa\delta} \cdot \Sigma (Q \log r) \dots \dots (17)$$

Since, for a given set of poles,  $\Sigma \phi$  is constant, this gives for a locus of constant potential

$$\Sigma (Q \log r) = \text{const.} = 2\pi\kappa\delta (\Sigma \phi - U),$$

which is in accordance with (16); for we may write

$$\Sigma \phi - U = n \Delta v,$$

and by § 8, when  $Q=1$ , we have  $\log \mu = 2\pi\kappa\delta \cdot \Delta v$ .

34. As already observed (§ 1), both the general equations

$$\Sigma(Q\theta) = \text{const. and } \Sigma(Q \log r) = \text{const.}$$

were given thirty years ago by Kirchhoff, who obtained the former as a purely mathematical consequence of the latter. In fact, as the systems of lines represented by them are orthogonal to each other, it follows that their first derived functions differ only in one having  $\frac{dy}{dx}$  where the other has  $-\frac{dx}{dy}$ ; hence differentiation and subsequent integration, after making this substitution, convert one expression into the other\*. This relation between the two equations is of importance, since the form of the equipotential lines can be readily determined experimentally, whereas no practicable method exists for ascertaining experimentally the course of the lines of flow.

35. Before going further we may point out some general properties of lines of flow and equipotential lines. Physically considered, a line drawn from any one pole to any other, so that no electricity crosses it at any point, may be regarded as an independent line of flow, as was done in treating the case of two equal and opposite poles. The lines, however, given by the equation  $\Sigma(Q\theta) = \text{const.}$  are continuous curves each of which passes through every pole; and, in a mathematical sense, the whole of the curve given by any one value of the constant must be regarded as a single line of flow. When flow-lines are spoken of in the sequel, it is to be understood that they are *complete* in the above sense. If all the poles are of equal strength, every flow-line passes once through each of them; hence, if they are unequal, every line passes through each of them respectively as

\* Let the coordinates of the several poles be  $(a_1, b_1), (a_2, b_2), \&c.$  The distances of a point from each will be  $r_1 = \sqrt{(x-a_1)^2 + (y-b_1)^2}, r_2 = \&c.,$  and the angles which the joining lines make with the axis of  $x$  will be given by  $\tan \theta_1 = \frac{y-b_1}{x-a_1}, \tan \theta_2 = \&c.$  Then

$$\begin{aligned} \frac{d}{dx} \Sigma(Q \log r) &= \Sigma \cdot Q \frac{d}{dx} \log \sqrt{(x-a)^2 + (y-b)^2} \\ &= \Sigma \cdot Q \left\{ \frac{x-a}{(x-a)^2 + (y-b)^2} + \frac{y-b}{(x-a)^2 + (y-b)^2} \cdot \frac{dy}{dx} \right\}. \end{aligned}$$

Now make the substitution, equivalent to writing  $\phi + \frac{\pi}{2}$  for  $\phi$ , and integrate,

$$\begin{aligned} \int \Sigma \cdot Q \left\{ \frac{y-b}{(x-a)^2 + (y-b)^2} - \frac{x-a}{(x-a)^2 + (y-b)^2} \cdot \frac{dy}{dx} \right\} dx \\ = \Sigma \cdot Q \tan^{-1} \frac{y-b}{x-a} = \Sigma(Q\theta). \end{aligned}$$

often as it contains the greatest common measure of the strengths of the whole set. Moreover, if on any flow-line there is a point of no flow, the line will intersect itself at this point one or more times. Separate flow-lines cannot intersect each other anywhere except at a pole.

Equipotential lines form closed curves which always surround one or more poles. At points where the strength of the current is nothing, the same equipotential line cuts itself once or oftener; in such cases there is at least one pole within each loop formed by the line. Separate equipotential lines never intersect each other.

The method of superposition, by which any system of flow-lines or equipotential lines can be drawn, is easily carried out by drawing, in rather strong lines on white paper, one of any two systems that are to be compounded to a resultant system, and drawing the other component system on tracing-paper. Placing the two drawings one over the other in any required manner, and laying a second piece of tracing-paper on the top, the curves which pass through the intersections of the two component systems can be drawn at once. The resultant system may then, if required, be recompounded with one of the components by the same process.

36. The general course of the lines of flow and equipotential lines for a few of the simpler cases is shown in Plate X.

*Two equal similar poles* (fig. 3).—The equation to the lines of flow for this case is

$$\theta_1 + \theta_2 = n\alpha,$$

which is equivalent to

$$x^2 - y^2 - 2xy \cot n\alpha = a^2,$$

if the straight line through the poles is taken as the axis of  $x$ , and its middle point as the origin. They are a system of rectangular hyperbolæ cutting each other at the poles with a constant difference of angle ( $=\alpha$ ). The value  $n\alpha = \pi$  gives the two axes, the origin where they intersect being a point of no flow. The equipotential lines for the same case are a system of lemniscates,  $r_1 r_2 = \mu^n$ , and are identical with the loci of equal flow for two equal opposite poles (§ 15). The strength of the current at any

point at a distance  $r$  from the origin is  $s = \frac{Q}{\pi} \cdot \frac{r}{r_1 r_2}$ ; and consequently

the loci of constant flow are the same as the equipotential lines for three equal poles—two of the same sign, and one of the opposite sign halfway between them, as shown in fig. 4. The strength of the current on the self-cutting curve is  $\frac{Q}{2\pi a}$ . For all other

values of  $s$  the curve consists of two separate branches; when  $s$

is  $> \frac{Q}{2\pi a}$ , one branch encloses each pole; and when  $s$  is  $< \frac{Q}{2\pi a}$ , one branch surrounds both poles and the other surrounds neither, being within the central loop of the self-cutting curve. Each of the loci cuts any straight line through the origin harmonically with respect to its intersection with the circle  $r=a$  and to the origin.

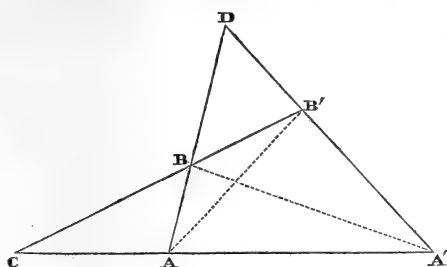
*Three equal poles.*—A special case coming under this head, which admits of some important applications, is that in which there are three equal poles in a straight line, one of the outside ones being of opposite sign to the other two—for instance, two sources A and A', and one sink C. In this case the flow-line given by  $\theta_1 + \theta_2 - \theta_3 = \pi$  consists of two branches, one of which is the flow-line passing through the poles; while the other is a circle whose centre is the sink C (fig. 5), and whose radius CP is a mean proportional between the distances from the sink to the two sources respectively (or  $CP = \sqrt{CA \cdot CA'}$ ). If the two sources coincide, the systems of lines of flow and equipotential lines become what are shown in fig. 6, and the circular branch of the flow-line  $n\alpha = \pi$  passes through the pole of double strength. In accordance with what was said above (§ 34), every flow-line of the system passes twice through the double source and once through the sink.

*Four equal poles.*—Four equal poles of the same sign situated at the corners of a square give the system of flow-lines represented in fig. 7. The two diagonals of the square and the two straight lines through the middle point parallel to the sides of the square are given equally by the values  $n\alpha = \pi$  and  $n\alpha = 0$ . For  $n\alpha = \frac{1}{2}\pi$  we get a curve of four branches, one of which is situated symmetrically in each quadrant.

A special case of four equal poles, which is important in consequence of its being susceptible of experimental verification, is presented by a combination of two sources and two sinks arranged in a manner that may be regarded as a duplication, with inversion of signs, of the system of three poles shown in fig. 5. Let the pole at C be a sink, those at A and A' being sources. Let two additional sinks be placed at B and B' (fig. 8), points on another straight line through C, and let a source equal to them be put at C; then the three poles of this new system would give by themselves, as one of their flow-lines, the straight line CB and the circle with centre C and radius  $= \sqrt{CB \cdot CB'}$ . If, however, the three new poles be made equal to the three poles of the first set, the sink originally at C and the equal source now put there will exactly compensate each other, and the combined system will be reduced to two sources at A and A' and two sinks

equal to them at B and B'. If, further, the points B and B' be taken so that  $CB \cdot CB' = CA \cdot CA'$ , the circle of radius CP will

Fig. 8.



be a common line of flow in each of the systems due to C, A, and A' and to C, B, and B', and will therefore remain a line of flow in the resultant system (see fig. 9) due to A, A', B, and B'. Moreover, since these four points are placed so that one circle can be drawn through them all, it is easy to see that this circle will be another flow-line of the resultant system; for the four poles may be grouped in two ways into two pairs of equal opposite poles (either A, B and A', B', or A, B' and A', B), each of which would separately give this circle as a line of flow. If the straight lines AB and A'B' are drawn and produced to their intersection at D (fig. 8), a circle drawn about this point as centre with radius  $= \sqrt{DB \cdot DA} = \sqrt{DB' \cdot DA'}$  will be an equipotential line common to the systems due respectively to the source and sink at A and B, and to those at A' and B'; consequently this circle is also an equipotential line of the resultant system due to all four poles. Another equipotential line of the resultant system would be the circle (in this case imaginary) drawn with the point of intersection of AB' and A'B as centre so as to cut each of these straight lines in points harmonically situated with respect to their extremities.

Again, if four equal poles be taken situated as in the last example, but so that poles of the same sign are diagonally opposite each other—in other words, if the signs of either A and B or of A' and B' be interchanged, the circle passing through the four poles will still be a flow-line of the resultant system, but C, as well as D, will now be the centre of an equipotential circle, while the imaginary circle will be a line of flow.

37. *Resistance.*—Equation (17) gives, for the difference of potential of any two points whose respective distances from the several poles are  $r_1, r_2, r_3, \dots$ , and  $r'_1, r'_2, \dots$  the value

$$2 K 2$$

$$U - U' = \frac{1}{2\pi\kappa\delta} [\Sigma(Q \log r') - \Sigma(Q \log r)]$$

$$= \frac{1}{2\pi\kappa\delta} \Sigma \left( Q \log \frac{r'}{r} \right),$$

since, for each pole, there are the corresponding terms  $Q_n \log r_n$  and  $Q_n \log r'_n$ . If there are altogether  $K$  poles,  $k$  being of one sign and  $k'$  of the opposite sign, where  $k$  is not less than  $k'$ , and if, further, they are all of the same strength, the quantity of electricity crossing each complete equipotential line in unit of time is  $kQ$ ; consequently the resistance of the portion of the sheet lying between the equipotential lines which pass through the given points is

$$R = \frac{U - U'}{kQ} = \frac{1}{2\pi\kappa\delta \cdot k} \cdot \Sigma \left( \log \frac{r'}{r} \right). \quad . \quad . \quad (18)$$

This formula is in principle quite general; but the practical application of it in actual cases requires that we should know the position of the poles from which the distances  $r_1, r_2, \dots$  are to be measured; and these cannot be ascertained (or at least not by elementary methods), except for comparatively few and simple cases; for although it is comparatively easy to determine the equipotential lines for a given set of poles, the inverse problem, of finding the distribution of poles required to produce equipotential lines coinciding with two given curves on the conducting sheet, presents in general very great mathematical difficulties, and has hitherto received only partial solutions.

38. We will give here, in the first place, the approximate application of the general formula to the case of two sources and two equal sinks at the angles of a quadrilateral inscribed in a circle and so placed that unlike poles are diagonally opposite each other. This is the arrangement shown in figs. 8 and 9, where  $A$  and  $A'$  may be taken as sources and  $B$  and  $B'$  as sinks. It is evident that the equipotential lines very near the poles will each consist of two branches, one of them surrounding one source (or sink), and the other surrounding the other source (or sink), and also that they will be very approximately circles having the poles at their centres. Hence, if the sources and sinks are formed by four circular electrodes, whose common radius  $\rho$  is a small fraction of the distance between any two of them, and if they are so placed that the distances of their centres  $A, A', B,$  and  $B'$  from a fixed point  $C$  fulfil the condition  $CA \cdot CA' = CB \cdot CB'$  (which is equivalent to saying that their centres are on the circumference of one and the same circle), we may without serious error regard the circles of contact between the electrodes and the conducting sheet as forming together a pair of equipotential lines due to such



a distribution of poles as that referred to at the beginning of this paragraph. Then, taking points on the circumference of the circles round A and B as the points to which the values of  $r$  and  $r'$  in equation (18) respectively refer, we have approximately

$$\Sigma \left( \log \frac{r'}{r} \right) = \log \frac{(AB)^2 \cdot AB' \cdot A'B}{\rho^2 \cdot AA' \cdot BB'};$$

and since for the case supposed  $k=k'=2$ , the resistance of the part of the sheet extending between the pair of circles round A and A' and the pair round B and B' is represented with similar approximation by

$$R = \frac{1}{4\pi\kappa\delta} \cdot \log \frac{(AB)^2 \cdot AB' \cdot A'B}{\rho^2 \cdot AA' \cdot BB'} \dots \dots (19)$$

If a circle be drawn with the centre C and radius

$$CP = \sqrt{CA \cdot CA'} = \sqrt{CB \cdot CB'},$$

this circle will coincide, as already pointed out (§ 35), with a flow-line of the system due to the combined action of the four poles. Consequently no electricity passes into or out of this circle; and therefore the whole of the electricity supplied by the source A flows to the sink B *inside* the circle (fig. 9), while the whole of what is supplied by the source A' flows to B' *outside* the circle. It follows, since the sources A and A' were assumed of the same strength, that the resistance offered by the part of the sheet lying within the circle of radius CP to the flow of electricity between the electrodes A and B is the same as the resistance of the part of the sheet lying outside this circle to the flow of electricity between the electrodes A' and B'. Hence also the resistance of a disk bounded by the circle in question and containing the two electrodes A and B is equal to *twice* the resistance of the entire sheet to all four poles, and is therefore represented by

$$R' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{(AB)^2 \cdot AB' \cdot A'B}{\rho^2 \cdot AA' \cdot BB'}, \dots \dots (20)$$

which is the formula referred to in § 1 (page 387) as having been given by Kirchhoff for the resistance of a circular disk with two small circular electrodes anywhere upon it.

39. As already stated, this formula is only approximate, and in certain special cases it entirely fails. For instance, if one (or both) of the poles passes to the edge of the disk, then, in order that the circumference may still continue to be a line of flow, the second pole of the same sign must coincide with it; consequently in such a case AA' or BB', or both, will vanish, and the expression for the resistance fails by becoming infinite. The reason evidently is that equation (20) was got by assuming  $\rho$  to

be very small in comparison with any of the distances between the poles; and this can no longer be true when any two of them coincide. By slightly modifying the notation, we can obtain an expression which does not fail in the same way. Thus, let the points to which the values of  $r_1, r_2, \dots$  refer be respectively a point F where the straight line AB cuts the equipotential circle round A, and a point G where the same line cuts the equipotential circle round B. Then we have  $AF = BG = \rho$ , and the expression for the resistance of the sheet to the current from all four poles becomes

$$R = \frac{1}{4\pi\kappa\delta} \cdot \log \left( \frac{BF \cdot B'F}{AF \cdot A'F} \cdot \frac{AG \cdot A'G}{BG \cdot B'G} \right), \quad (19a)$$

while the resistance of the disk bounded by the circular flow-line may be written

$$R' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{AG \cdot BF \cdot A'G \cdot B'F}{\rho^2 \cdot A'F \cdot B'G}. \quad (20a)$$

In this form the expression for  $R'$  admits of extension to some special cases. For example, let the pole A pass to the edge of the disk, while B goes to the centre; then  $A'$  will coincide with A, and  $B'$  will go to an infinite distance. We have then sensibly  $AG = BF = A'G =$  the radius of the disk ( $= P$ ), also  $A'F = \rho$ , and the resistance to the flow between the pole at the edge and the pole at the centre of the disk becomes

$$\frac{3}{2\pi\kappa\delta} \cdot \log \frac{P}{\rho} \dots \dots \dots (21)$$

If both poles go to the edge,  $A'$  coincides with A, and  $B'$  with B, the system being reduced to two equal opposite poles at a distance  $AG = BF = 2a$  from each other. In accordance with this, the resistance of the whole sheet becomes

$$\frac{1}{\pi\kappa\delta} \cdot \log \frac{2a}{\rho},$$

which is the value already given for the same case in equation (8).

40. If, all else remaining as before, the signs of the poles  $A'$  and  $B'$  are interchanged (that is, if  $A'$  becomes a sink and  $B'$  a source), the circle drawn with the centre C and radius  $\sqrt{CA \cdot CA'}$  becomes an equipotential line instead of a line of flow, the circle with centre D and radius  $\sqrt{DB \cdot DA}$  remains an equipotential line, and the only circular lines of flow are the circle through the four poles and the imaginary circle (§ 36) whose centre is the intersection of  $AB'$  and  $A'B$ . The resistance of the sheet to the flow of electricity between this new arrangement of poles is given by interchanging in (19a) the signs of the *radii vectores* drawn

from A' and B', whereby we get

$$R = \frac{1}{4\pi\kappa\delta} \cdot \log \frac{AG \cdot BF \cdot A'F \cdot B'G}{\rho^2 \cdot A'G \cdot B'F}. \quad (19b)$$

The equipotential circles with the centres C and D being common to the system due to the source at A and sink at A', and also to that due to the sink at B and source at B', and having equal but opposite potentials when taken as belonging to either of these systems separately, will, in the system due to the four poles, form the two branches of the line of zero potential. The other equipotential lines of the system due to the four poles consist also each of them of two branches, both of which never lie within the same one of the two circles in question. From this it follows that each circle divides the sheet into two equiresisting portions; and consequently the resistance of each of them is

$$R'' = \frac{1}{2\pi\kappa\delta} \cdot \log \frac{AG \cdot BF \cdot A'F \cdot B'G}{\rho^2 \cdot A'G \cdot B'F}^*. \quad (22)$$

41. Since half the lines of flow due to each pole lie within the circle drawn through them all, the resistance of the portion of the sheet bounded by this circle is (§ 25) twice the resistance of the unlimited sheet; consequently it is equal to R' or to R'' according to the arrangement of the poles.

42. It was pointed out in § 39 that the resistance of the part of the sheet outside the circular flow-line with centre C, to the flow from the source A' to the sink B', is the same as the resistance of the part inside this circle to the flow from A to B. Accordingly the value of equation (20) remains unaltered when A' and B' are put for A and B, and *vice versa*, and at the same time  $\rho^2$  (or  $\rho_A \rho_B$ ) is replaced by  $\rho_A \rho_{B'} = \rho_A \rho_B \left( \frac{A'B'}{AB} \right)^2$ . The

circles round the two sources then coincide approximately with the two branches of a single equipotential line; and the same is true for those surrounding the sinks.

Similar remarks are applicable to equation (22).

Experimental verifications of some of the conclusions here arrived at will be given in Part II. of this communication.

\* It may be noted that by adding together the values of R' and R'' we get  $\frac{1}{2\pi\kappa\delta} \cdot \log \left( \frac{AG \cdot BF}{\rho^2} \right)^2$ , which, written in the simpler form

$$\frac{2}{\pi\kappa\delta} \cdot \log \frac{AB}{\rho},$$

is the resistance of a circular disk on whose edge the poles A and B are placed (see equation 13).

Errata in No. 326.

Page 395, line 3, *for in read on*.

— 398, line 17, *for from line read from one line*.

LIV. *On a new Revolving Polariscopes.*  
 By WILLIAM SPOTTISWOODE, M.A., F.R.S.\*

**T**HIS instrument consists of a Nicol's prism or other ordinary polarizer, and a double-image prism as analyzer. The latter is so cut as to show one image in the centre of the field of view, the other excentric; and the peculiarity of the arrangement consists in giving to the analyzer a rapid motion of rotation. If the speed attains eight or ten revolutions per second, the image will remain persistently upon the retina during an entire revolution, and all the phenomena which are usually seen in succession will appear displayed simultaneously in a circle or ring by the excentric image.

The central image will consist of a superposition of the images due to all the successive azimuths of the analyzer, and will consequently appear unchanged in brightness or in colour during the working of the instrument.

In particular, if the polarizer and analyzer be used without any interposed plate, the excentric image will as usual be brightest at two positions opposite to each other, say at  $0^\circ$  and  $180^\circ$ , and dark at the two positions  $90^\circ$  and  $270^\circ$ . A rapid revolution of the analyzer will therefore give the appearance of a ring brightest at the two positions first mentioned, and fading into darkness at the two other positions.

If a plate of selenite be interposed with its axis at  $45^\circ$  to the original plane of polarization, the two images will present complementary tints at  $0^\circ$  and  $180^\circ$ , and likewise at  $90^\circ$  and  $270^\circ$ ; but at the two latter positions the tints will be the reverse of those at the two former. At intermediate positions the tints will be fainter, while  $45^\circ$  and  $135^\circ$  will be positions at which each tint is passing into its complementary, and all colour is lost. In this case, therefore, the ring will appear coloured in opposite quadrants with the same tint, in the intermediate quadrants with the complementary tint. In the intervening parts the tints fade into one another.

If a plate of quartz cut perpendicularly to the axis be used instead of the selenite, the entire series of spectral tints will be seen displayed twice over in the ring. The order of the tints in the ring will for a given direction of revolution depend upon the character of the quartz, *i. e.* whether it is positive or negative.

Some interesting experiments may also be made with a quarter-undulation plate. By this means plane polarization may, as is well known, be converted into circular, and circular into plane. Hence, if we place a quarter-undulation plate in front of a selenite, we shall produce the complete series of tints in the ring, as

\* Communicated by the Author

with a quartz plate. The order of the tints will be that due to a right-handed quartz for one position of the quarter-undulation plate, and will be that due to a left-handed quartz for a position at right angles to the first.

In order that this effect may be successfully produced, the thicknesses of the selenite and quarter-undulation plate must be adapted to one another. The latter is usually constructed for the yellow rays; and with such plates we should consequently use a selenite giving yellow and blue images.

If the quarter-undulation plate be used with a quartz perpendicular to the axis, the tints may be reduced to a pair of complementaries, as given by a selenite.

To these many other and varied experiments may be added, but on the present occasion I will confine my remarks to two of them.

In the cases hitherto described the central image appears colourless and uniformly illuminated, while the excentric image or ring has been the chief subject of observation. But if instead of a plane plate we use quartz wedges giving Savart's bands, or a concave quartz cut parallel to the axis, the central image will be the most interesting. We shall then see light and dark (or coloured and colourless) bands taking alternate places at each half revolution of the analyzer. The ring shows no very striking feature. If a quarter-undulation plate be used, the bands will be seen to travel across the plate, in one direction when it is placed so as to produce right-handed, or in the other when placed so as to produce left-handed circular polarization.

Analogous effects are seen with a concave quartz plate cut parallel to the axis. The central figure then shows rings, which with a quarter-undulation plate expand or contract according to the position of that plate. When, however, the analyzer revolves rapidly, it will be noticed that the rings assume the form of spirals. This is due to the fact that the central image, when produced by a circularly concave plate, is not accurately circular, but elliptical, owing to the unequal refraction of the double-image prism in two rectangular directions. To the same cause is attributable the apparent wabbling of the central image, even when the instrument is in perfect adjustment.

The principle of the revolving analyzer is applicable alike to a table polariscopes for eye-observations and to one constructed for projection. In the table polariscopes it is used above the analyzer, a diaphragm being placed immediately over the object on the stage of the instrument; in that for projection it may be placed in the focus of the focusing-lens of the system.

LV. *Proceedings of Learned Societies.*

## ROYAL SOCIETY.

[Continued from p. 326.]

June 18, 1874.—Joseph Dalton Hooker, C.B., President, in the Chair.

THE following communication was read:—

“On the Sun-spot Period and the Rainfall.” By J. A. Broun, F.R.S.

Having read with much interest Mr. Meldrum’s communication to the Royal Society on the apparent simultaneity of excess of rainfall and sun-spot area\*, I have waited some confirmation of his conclusions from a more extensive induction. Mr. Hennessey’s “Note” in the Proceedings of the Society for April 1874† induces me to offer the following views and results to the Royal Society.

It is well known that the amount of rainfall is a very variable quantity in some countries and in certain positions, and that when there is a year of drought in one part of the world, there is frequently an excess of rain in another. Any investigation, then, which should be occupied with the average fall of rain over the earth’s surface must be long and laborious, unless the variation to be dealt with is large and marked compared with others which must be considered purely accidental relatively to the sun’s spots. In proof of this I may cite the rainfall at Mussoorie given by Mr. Hennessey‡, where, as far as the sun-spot area is known, any result favourable to the connexion of the two phenomena depends wholly on the rainfall for 1861, which is upwards of 50 inches in excess of the mean. If this excess be not due to the great spot-area, then a long series of years’ observations might be requisite to make the positive and negative errors destroy each other.

It has been with the intention of determining what may be the effect of a given change of sun-spot area, within a limited district, during a period favourable to the connexion of the two phenomena, that the following discussions have been made. We can then say approximately within what limits the excess and deficiency of rainfall lie for the years of greatest and least spot-area, what amount of observations may be required to destroy accidental variations, and whether the result may encourage more extensive research.

Mr. Meldrum finds a *mean* difference of 8·5 inches of rain between the falls for the years of greatest and least spot-area§; but this result is derived to some extent from short series of observations made in different parts of the world, and gives no weight to the rainfall in other years than those considered years of maximum or minimum sun-spots.

\* Proceedings of the Royal Society, vol. xxi. p. 297.

† *Ibid.* vol. xxii. p. 286. ‡ *Ibid.* vol. xxii. p. 287. § *Ibid.* vol. xxi. p. 305.

Should there be any connexion betwixt the rainfall and spot-area, we may always in the first instance represent it approximately by an equation of this form,

$$\Delta R = f \Delta A,$$

where  $\Delta R$  is the excess or deficiency of the rainfall from the mean,  $\Delta A$  is the excess or defect of spot-area for the same period of time, and  $f$  is a constant to be deduced from the observations.

Having obtained the mean spot-area for each year from 1832 to 1867, from Table VII. of the paper on this subject by Messrs. De La Rue, Stewart, and Loewy\*, the mean for three periods of 11 years (1832 to 1864) was found equal to 643 millionths of the sun's visible surface; with this quantity the values of  $\pm \Delta A$  (in millionths of the sun's surface) for each year were obtained.

Mr. Meldrum's conclusion depends chiefly on observations during these periods in Great Britain; and as he has deduced the rainfall for the first period of minimum spots from observations at three stations, Greenwich, Carbeth (near Glasgow), and Aberdeen, I first examined the observations at these places together with simultaneous observations at Makerstoun for the two periods 1832 to 1853†. Applying the above equation to these observations, the following results were obtained:—

Greenwich . . . . .	$\Delta R = -0.00092 \Delta A$ ;
Makerstoun . . . . .	$\Delta R = -0.00020 \Delta A$ ;
Carbeth . . . . .	$\Delta R = +0.00158 \Delta A$ ;
Aberdeen . . . . .	$\Delta R = +0.00128 \Delta A$ .

Greenwich and Makerstoun are thus opposed to the conclusion, and Carbeth and Aberdeen are more strongly in its favour. It should be remarked, however, that the result for Aberdeen depends wholly on the rainfall given for that place in 1834 (12.3 in.) being exact. As it is 12 inches less than the mean, while at the other three stations the deficiency is only from 0.6 in. at Greenwich and Makerstoun to 1.2 in. at Carbeth, this may be due to a leaky rain-gauge or to a clerical error of 10 inches. In any case no great weight can be given to the conclusion from these four stations‡.

I now sought for an approximation to the mean fall of rain for Great Britain, and for this end have employed the quantities de-

\* Phil. Trans. 1870, p. 399.

† The means for Makerstoun during the years 1832 to 1849 will be found in Trans. Roy. Soc. Edinb. vol. xix. pt. ii. p. 108; the falls for the other years are—1850, 21.49 in.; 1851, 25.57 in.; 1852, 32.20 in.; 1853, 23.54 in.

‡ It may here be noted that the sum of the *plus* and *minus* differences of  $R$  and the mean rainfall for the four stations during the twenty-two years were—

	Greenwich.	Makerstoun.	Carbeth.	Aberdeen,]
Mean fall.....	24.4 in.	26.2 in.	43.6 in.	24.2 in.
Sums of $\Delta R$ .....	100.1 in.	67.8 in.	92.4 in.	94.3 in.

It will be seen that the sums of differences have no relation to the mean fall of rain.

duced by Mr. Symons from ten stations (British Association Report, 1865, p. 203; 1871, p. 102). The differences of spot-area from the mean, in millionths of the sun's surface, and of the rainfall for each year are given in the following Table:—

Differences of Rainfall for Great Britain and of Sun-spot area for 1832 to 1867.

Year.	$\Delta A.$	$\Delta R.$	Year.	$\Delta A.$	$\Delta R.$	Year.	$\Delta A.$	$\Delta R.$	Means.	
									$\Delta A.$	$\Delta R.$
		in.			in.			in.		in.
1832.	−359	−1·54	1843.	−540	+2·66*	1854.	−501	−5·36	−467	−1·41
1833.	−558	+1·97*	1844.	−465	−4·02	1855.	−566	−4·47	−540	−2·17
1834.	−506	−3·22	1845.	−232	+0·13*	1856.	−619	−1·85	−452	−1·64
1835.	+171	+0·82	1846.	−5	+1·83*	1857.	−428	−2·04	−87	+0·20
1836.	+746	+5·75	1847.	+469	−1·94*	1858.	+177	−4·95*	+444	−0·38
1837.	+556	−3·20*	1848.	+395	+8·24	1859.	+756	+0·79	+569	+1·94
1838.	+293	−0·63*	1849.	+203	+0·77	1860.	+656	+5·60	+384	+1·91
1839.	+164	+3·53	1850.	−123	−1·39	1861.	+659	−0·76*	+267	+0·46
1840.	−46	−3·07	1851.	+40	−1·04*	1862.	+530	+2·63	+174	−0·49
1841.	−306	+5·77*	1852.	−92	+7·79*	1863.	−15	−0·81	−138	+4·26
1842.	−429	−2·21	1853.	−253	−0·36	1864.	+245	−5·63*	−146	−2·73
						1865.	−187	+1·90*	−409	−0·27
						1866.	−342	+3·26*	−458	−1·74
						1867.	−468	+0·70*	−440	−0·34

If we seek the value of  $f$  for the mean of the three periods of eleven years commencing 1832 and 1835, we find the following equations:—

$$1832 \text{ to } 1864 \dots\dots\dots \Delta R = +0\cdot0019 \Delta A;$$

$$1835 \text{ to } 1867 \dots\dots\dots \Delta R = +0\cdot0011 \Delta A.$$

These results, then, are, as we expected, in conformity with Mr. Meldrum's conclusion; so that if we compare the year of largest with that of smallest spot-area, the difference of rainfall should amount to 2·61 in. by the first and to 1·51 in. by the second value of  $f$ . If we take the mean spot-area for the years 1834, 1844, 1856, and 1866, and for 1836, 1848, and 1861, we find that the mean difference of rainfall for these years should be 2·06 in. by the first and 1·20 in. by the second value of  $f$ , instead of 8·45 in. as found by Mr. Meldrum.

It will be seen also that the greatest mean difference of rainfall is that for the years 1841, 1852, and 1863, and this was an excess of rain for years of spot-area deficiency; were another such opposite difference to present itself, it would neutralize the conclusion derived from these means. It should also be observed that while the first and third periods of eleven years are in favour of the connexion, the second (1843 to 1853) is opposed to it (this is also the case for the eleven years 1857 to 1867).

It will be seen, then, that from this discussion a probable

\* Indicates opposite signs of  $\Delta A$  and  $\Delta R$ .



difference of about 2 inches of rain may be expected betwixt years of greatest and least spot-area.

This result is derived from observations at ten stations, distributed over a very small patch of the earth's surface; and it is evident that for any serious investigation a much larger series of observations representing the rainfall over a great extent of country would be essential.

I now examined observations made at different stations in India; but this examination showed the extreme difficulty of obtaining a satisfactory result, either way, from a few stations in that country, when, in certain years, the accidental excess of rainfall at some of the stations may be 40 inches, even though deficiencies at some stations may diminish the amount of the error.

From my own experience of rainfall on the Indian ghats, I should doubt that a mountain-station, such as Mussoorie, is well fitted to be employed in this discussion. If a single station could be taken to represent any tract of country, it ought to be one least liable to local causes of variation. Among the mountains a slight change in the average direction of the wind will cause great differences in the rainfall at stations but little distant from each other, and to eliminate accidental variations of 40 or 80 inches would require observations during a very long series of years.

The following Table will, however, show the quantities which may have to be dealt with at an Indian hill-station†:—

Values of  $\Delta R$  for Mahabuleshwar, 4500 feet above the sea, with the corresponding values of  $\Delta A$ .

Year.	$\Delta A$ .	$\Delta R$ .	Year.	$\Delta A$ .	$\Delta R$ .
		in.			in.
1832.	—359	—26·1	1843.	—540	+32·7*
1833.	—558	—49·3	1844.	—465	+ 9·3*
1834.	—506	+44·3*	1845.	—232	— 3·1
1835.	+171	—26·3*	1846.	— 5	+35·3*
1836.	+746	— 9·4*	1847.	+469	—34·2*
1837.	+556	+14·8	1848.	+395	— 8·0*
1838.	+293	—72·8*	1849.	+203	+85·4
1839.	+164	—19·8*			
1840.	— 46	+31·4*			
1841.	—306	+28·0*			
1842.	—429	+51·9*			

From this Table we derive the equation]

$$\Delta R = -0\cdot02 \text{ in. } \Delta A,$$

or that 26 inches *more* rain falls for the year of *least* than for

† For the rainfall at Mahabuleshwar, see Colonel Sykes's paper on Indian observations, Phil. Trans. 1850, p. 367. The mean fall is 253·0 inches.

\* Indicates opposite signs of  $\Delta A$  and  $\Delta R$ .

that of greatest spot-area. The examination of many series of observations has shown how difficult it will be to arrive at a conclusion for a quantity so small as 2 inches of rain.

It is evident that a larger tract of country than Great Britain should be chosen, and the approximate rainfall be deduced from the greatest possible number of stations. Germany and France may give sufficient data for such a trial. Were the result well marked, there would be reason to seek for its confirmation in other countries; but to undertake this labour, better grounds, I think, must be found than I have hitherto been able to obtain. The admirable series of observations which Mr. Symons is obtaining will suffice for the future, as for the past, ten years to give a very near approximation to the excess or deficiency of rainfall in Great Britain.

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GEOLOGICAL SOCIETY.

[Continued from p. 410.]

June 24, 1874.—John Evans, Esq., F.R.S., President,  
In the Chair.

The following communications were read:—

1. “New Carboniferous Polyzoa.” By Prof. John Young, M.D., F.G.S., and John Young, Esq., F.G.S., Hunterian Museum, Glasgow University.

The authors described two new forms of Polyzoa from the Carboniferous Limestone shales near Glasgow. For one of these they proposed to form a new genus, *Actinostoma*, allied to *Fenestella*, with the frond erect, and poriferous on one face only, and with the fenestrules oblong. The species they named *A. fenestratum*. The second species was described under the name of *Glaucanome stellipora*.

2. “On *Palæocoryne* and other Polyzoal Appendages.” By Prof. John Young, M.D., F.G.S., and John Young, Esq., F.G.S., Hunterian Museum, Glasgow University.

The authors maintained that the structures described by MM. Duncan and Jenkins under the name of *Palæocoryne*, are not independent organisms, but mere processes of the Polyzoa on which they occur, the cells at the base being only the cells of the Polyzoa. They stated that the tissues of the two structures are perfectly continuous, that the “dactylose basal lobes” are the branches of the Polyzoan of which the processes are continuations, that the stem, capitulum, and branches of the processes are solid, that there is no normal aperture in the capitulum, that the stems do not always bear capitula, even when they give off branches, and that in many cases they are mere processes without either capitulum or branches. According to their observations, the stellate processes called *Palæocoryne* are given off chiefly from the poriferous face, and the other processes from the poriferous and non-poriferous faces, and from the

edge and base of the frond. The authors did not express any positive opinion as to the function of these processes; but they suggested that those given off from the non-poriferous face and from the base of calycine fronds, may serve as adventitious roots, and those given off from the margins and from the poriferous face near the margins may be irregularities of growth, unless they are the commencement of new fronds.

3. "The Steppes of Siberia." By Thomas Belt, Esq., F.G.S.

The author described the portion of the Siberian steppes traversed by him as consisting of sand and loam. The best section seen by him was at Pavlodar, where he found 1 foot of surface soil, 20 feet of stratified reddish-brown sand, with lines of small gravel, 8 feet of light-coloured sandy silt, 15 feet of coarse sand, with lines of small pebbles and 1 line of large ones, and 6 feet of clayey un laminated silt, with fragments of the bed rock in its lower half, the bed rock being Magnesian Limestone much crushed at the top. South of Pavlodar the surface was covered with pebbles, which became larger in advancing southward, until the soil was full of large angular quartz boulders. Further south the bed-rock comes to the surface in ridges and low hills, increasing in height until some of them attain 2000 feet. All the rock-surfaces were much shattered, as if by the action of frost, but they showed no signs of glacier-action. The ridges and hills were separated by plains composed of sandy clay, with numerous angular fragments derived from the rocks in the immediate neighbourhood. This is accounted for by the author on the supposition that they formed a series of shallow lakes, frozen over in winter, and that the ice on breaking up carried away fragments of the rocks. The distribution of the boulders on the plain north of the ridges was also attributed to floating ice.

The generally accepted marine origin of the great plain was said to be negatived by the absence of sea-shells in its deposits, whilst *Cyrena fluminalis* occurs in them. The author regards them as deposits from a great expanse of fresh water kept back by a barrier of polar ice descending far towards the south. In its greatest extension this ice-barrier would produce the crushing of the bed-rock; and as it retreated, the water coming down from the higher ground in the south would cover a continually increasing surface.

4. "On the Microscopic Structure and Composition of British Carboniferous Dolerites." By S. Allport, Esq., F.G.S.

The object of this paper is to supply further and conclusive evidence to show that there are dolerites and basalts of Carboniferous age whose original mineral constitution is precisely the same as those of the later Tertiary periods, those of both ages presenting the same varieties of structure, and that the great alterations which most of the older rocks have undergone constitute the only difference between the two groups. The author describes at some length the various constituents under the following heads, viz. felspar, augite, olivine, magnetite, mica, apatite, glassy matrix, &c.

He next describes the occurrence of dolerites in the Midland Coal-fields, Ireland, Edinburgh, Arran, &c.

In conclusion he draws attention to the many variations in composition and texture in the same rock-mass, and accounts for them thus:—If the lava were simply in a viscid state, with the ingredients imperfectly mixed, portions of it must, on consolidation, contain them in various proportions, just as is known to be the case in imperfectly fused slags.

He maintains that there is an absolute identity of composition, structure, and mode of occurrence in these eruptive rocks of very widely separated geological periods, and that therefore they should be placed in one group.

5. "Additional Remarks on Boulders, with a particular reference to a group of very large and far-travelled erratics in Llanarmon parish, Denbighshire." By D. Mackintosh, Esq., F.G.S.

The author, after referring to a number of northern-drift boulders in addition to those he had noticed in a former paper, describes several large felspathic boulders found up to a height of about 1750 feet above the sea, on Cefn-y-fedw, N. of Llangollen. He then gives a somewhat detailed account of the drifts in the neighbourhood of Corwen, and of some large felspathic boulders, probably from the Arenig mountains, which are generally found on the surface, or interposed between the lower boulder-clay and an upland extension of the middle sand of the plains. The main part of the paper is devoted to an account of the discovery of a numerous group of very large and far-travelled felspathic boulders in the parish of Llanarmon, Denbighshire. The author refers particularly to a remarkable slickensided boulder, and to the great "Immovable Stone" at Maendigychwyn (now called Eryrys), about 1150 feet above the sea, which is the largest far-transported boulder he has heard of in the British Isles. He stated a number of facts and considerations which led him to believe that the Llanarmon boulders, along with those further N. and W., must have come all the way from Snowdon, and that they were floated over passes or cols in the intervening ranges of hills by icebergs or coast-ice about the close of the Lower Boulder-clay period. He concluded by noticing the necessity for a personal examination of boulders instead of relying on answers to queries, and stated that about Llanarmon the felspathic boulders are called "granite tumblers," while in Cheshire all kinds of boulders are called "marble stones."

6. "Note on the Bingera Diamond-fields." By Archibald Liveridge, Esq., F.G.S.

The author commenced by describing the general characters of the older Australian Diamond-field of the Mudjee or Cudgegong District. The Bingera Diamond-field is situated in a basin among the mountains of the Drummond range, the encircling hills being of Carboniferous or Devonian age. The diamantiferous drift occurs in patches in the basin, which is invaded by spurs of basalt. The

rock under the drift is an argillaceous shale; and here and there are outcrops of a siliceous conglomerate. The diamonds have hitherto been worked only at the surface. The author mentions the principal minerals found associated with the diamonds, which are generally small, and their crystalline forms not very well developed. He also remarks on the general accordance in the geological constitution of various diamantiferous districts.

7. "Remarks on the working of the Molar Teeth of the *Diprotodon*." By Gerard Krefft, Esq., F.L.S. Communicated by the President.

In this paper the author criticised a figure of the lower molars of *Diprotodon*, published by Professor Owen, on the ground that the teeth are represented in it in an unabraded state, and stated that when the last tooth breaks through the gum the first of the series is always worn flat. He also remarked on the peculiar modification of the premolar in the genus *Diprotodon*.

## LVI. Intelligence and Miscellaneous Articles.

### ON THE SPECTRUM OF THE AURORA.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

I AM obliged to Dr. Marshall Watts for pointing out the errors in the wave-lengths of the oxygen- and carbon-lines as compared in my paper. I am aware that in spectrum No. II. of the "Index" *j* is given as 5602; but I assumed this to be a misprint for 5622, as these last figures appear in spectrum No. I. against the same scale-reading, viz. 58. The wave-lengths in the blue and green were accidentally transposed. The true reading will therefore stand thus:—

	Yellow.	Green.	Blue.
Dr. Vogel's oxygen-lines .....	5603	5189	4829
Dr. Watts's carbon-lines .....	5602	5195	4834

I am aware of the frequent impurity of vacuum-tubes; but it is hardly probable all the oxygen-tubes examined were impure.

Dr. Vogel, too, does not hint at any suspicion of his tube, which, as I have said, agrees with mine very closely.

I am, &c.,

J. RAND CAPRON.

Guildford, May 1, 1875.

*Phil. Mag.* S. 4. Vol. 49. No. 327. June 1875. 2 L

## ON THE DETERMINATION OF THE QUANTITY OF MAGNETISM OF A MAGNET. BY R. BLONDLOT.

The notion of instituting a method of magnetic exploration based on the production of induced currents has long been entertained. In 1849 Van Rees published\* the result of researches on the distribution of magnetism, the principle of his process being as follows:—The wire of a much-flattened induction-coil is connected with a galvanometer; the bar to be examined is introduced into the coil up to a fixed point of the latter, and is then briskly withdrawn to a great distance: this gives rise to an induction-current, which deflects the needle of the galvanometer a certain angle.

Van Rees lays down a simple proportionality between the intensity of the current and the inducing magnetism, from which it follows that the current observed is a measure for the sum of the free magnetism over which the coil glides; and he concludes, from a known relation, that that sum is equal to the actual magnetism at the place from which the withdrawal of the coil started.

Subsequently, in 1861, in a memoir an abstract of which appeared in Poggendorff's *Annalen*†, M. Rothlauf treats the same subject, commencing with a critical examination of Van Rees's memoir. The theory of the latter is faulty in two points; the principal charge against it is that it supposes the experiments to be made with a coil formed of one circumvolution only, and that the points situated beneath it are the only ones which act by induction. We refer for the details of the criticism to M. Rothlauf's memoir‡.

Finally, M. Gaugain has recently taken up Van Rees's method, and made it the foundation of researches, which he is pursuing with success, on magnetism.

It appeared to us important to examine Van Rees's method from the theoretical point of view, to seek the exact signification of the numbers given by it, and to treat in particular a case in which, though generally inaccurate, its application does not involve any appreciable error.

The first impulse measured represents, with respect to the induced current, the integral  $\int_{t_0}^{t_1} i dt$ ,  $i$  denoting the variable intensity of the current, and  $t$  the time, the limits of which are  $t_0$  and  $t_1$ .

Let us go back to the theory of induction-currents given by Neumann.

If we have a fixed pole P, and a closed circuit B moving in relation to the pole, there is produced in the circuit an induction-current in the inverse direction of the current which would give to the circuit the motion which it actually has (Lenz's law).

Let  $ds$  be an element of the circuit; this element is the seat of an electromotive force  $eds$ . If the circuit B were traversed by a

\* Pogg. *Ann.* vol. lxxiv. p. 217.

† "Bestimmung der magnetischen Vertheilung mittelst Magnet-Induction," Pogg. *Ann.* vol. cxvi. p. 592.

‡ See also G. Wiedemann, *Die Lehre von Galvanismus*, vol. ii. p. 321, note.

current of the intensity  $m$  in absolute measure,  $ds$  would be acted on by a certain force from the pole  $P$ . Let  $\gamma$  be the component of that force along the direction of the motion; the elemental law given by Neumann is the following:—

$$e ds = -\epsilon v \gamma,$$

$v$  designating the velocity of the element  $ds$ , and  $\epsilon$  being a constant.

Let us consider what takes place in the time  $dt$  for the entire circuit. Let  $R$  be the resistance; the elementary current produced will be, according to Ohm's law,

$$i dt = -\frac{\epsilon}{R} \Sigma v \gamma dt,$$

the symbol  $\Sigma$  extending to the entire circuit  $B$ .

But we have  $v = \frac{dw}{dt}$ ,  $dw$  representing the element of the trajectory of  $ds$ ; therefore

$$i dt = \frac{\epsilon}{R} \Sigma \gamma \frac{dw}{dt} = -\frac{\epsilon}{R} \Sigma \gamma dw,$$

which gives the following enunciation:—

*The differential current is equal, except a factor, to the sum of the elementary work of the forces to which the pole is subjected on the part of the elements of a current 1 supposed to traverse the circuit B.*

Integrating between the corresponding limits, we get

$$\int_0^{t_1} i dt = -\frac{\epsilon}{R} \int_0^{w_1} \Sigma \gamma dw. \dots\dots\dots (A)$$

It follows that, for a given circuit, the first impulse of the galvanometer is proportional to the work which would be necessary to produce the relative motion of the pole and the circuit supposed to be traversed by the current 1.

If we wish to pass to the case of the true magnet, it suffices to consider any number of poles; and it is seen, by a series of summations, that the theorem applies in the case of any distribution as in that of a single pole.

We have now to estimate the work as a function of the data of experiment.

Let  $V$  be the potential, relative to the circuit, of any pole  $P$ , and  $\mu$  the magnetism of the pole; the work in order that the system may pass from one state to the other, taking into account this pole only, is equal to the corresponding variation of the quantity  $\mu V$ ; let it be  $\mu(V_1 - V_0)$ . We shall therefore have, by substitution in equation (A),

$$\int_{t_0}^{t_1} i dt = -\frac{\epsilon}{R} \Sigma \mu (V_1 - V_0),$$

the summation here extending to all the poles of the arrangement\*.

\* This equation agrees with the calculation given by G. Wiedemann, *l. c.* vol. iii. p. 80.

This relation, in general very complicated, is simplified in a special case, as we will show.

Let us consider the potential  $V$  of a pole  $P$ . It is known that this potential has for its value in absolute measure the opening of the cone under which the pole  $P$  regards the current. If, then, the circuit  $B$  starts from negative infinity to reach the pole and then remove thence to positive infinity, the potential varies by the quantity  $4\pi$ .

From this it follows that, in the above-indicated conditions of displacement,  $V_1 - V_0$  is a constant quantity, and equal to  $4\pi$  for all the poles; consequently it can be put as a factor, which gives

$$\int_0^{t_1} i dt = -\frac{e}{R} 4\pi \Sigma \mu = -\frac{e}{R} 4\pi M,$$

designating by  $M$  the total magnetism of the arrangement.

In a long magnet the magnetism can be regarded as collected in the vicinity of the extremities; therefore if the coil be placed on the middle portion of such a magnet and the latter be afterwards removed to a great distance, the conditions will be sensibly those of the preceding theory. It hence follows that the quantity of the current can serve for measuring the total magnetism of the half of a bar, provided that the bar be not too short—that is to say, that its polar distance be not less than 8–10 centims.

We see also that the current is independent of the diameter of the coil, if this diameter is a small fraction of the length of the bar. The last proposition was experimentally verified by Faraday and Lenz, and more recently by M. Gauguain.—*Comptes Rendus de l'Académie des Sciences*, vol. lxxx. pp. 653–656.

#### ON CAMACHO'S NEW ELECTROMAGNET.

*To the Editors of the Philosophical Magazine and Journal,*

GENTLEMEN,

In the April Number of your Magazine Mr. R. S. Culley states that he had in his possession, in 1852, a magnet similar in principle to that of M. Camacho, which was invented by the late Richard Roberts. I take the following extract from a paper on the Construction of Galvanic Magnets, by John B. Zabriskie, M.D., published in the American Journal of Science and Arts for July 1839. After dwelling upon the difficulty of "saturating with magnetism large masses of iron," he continues, "but if we divide perpendicularly each extremity of a large magnet into four equal parts and wind each part separately, there will be no difficulty in completely saturating the whole." This seems to me to be the same idea upon which both Mr. Roberts and M. Camacho proceeded to construct their magnets.

Yours sincerely,

JOHN TROWBRIDGE, S.D. Harv. Coll.

Cambridge, U. S.



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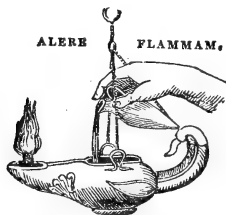
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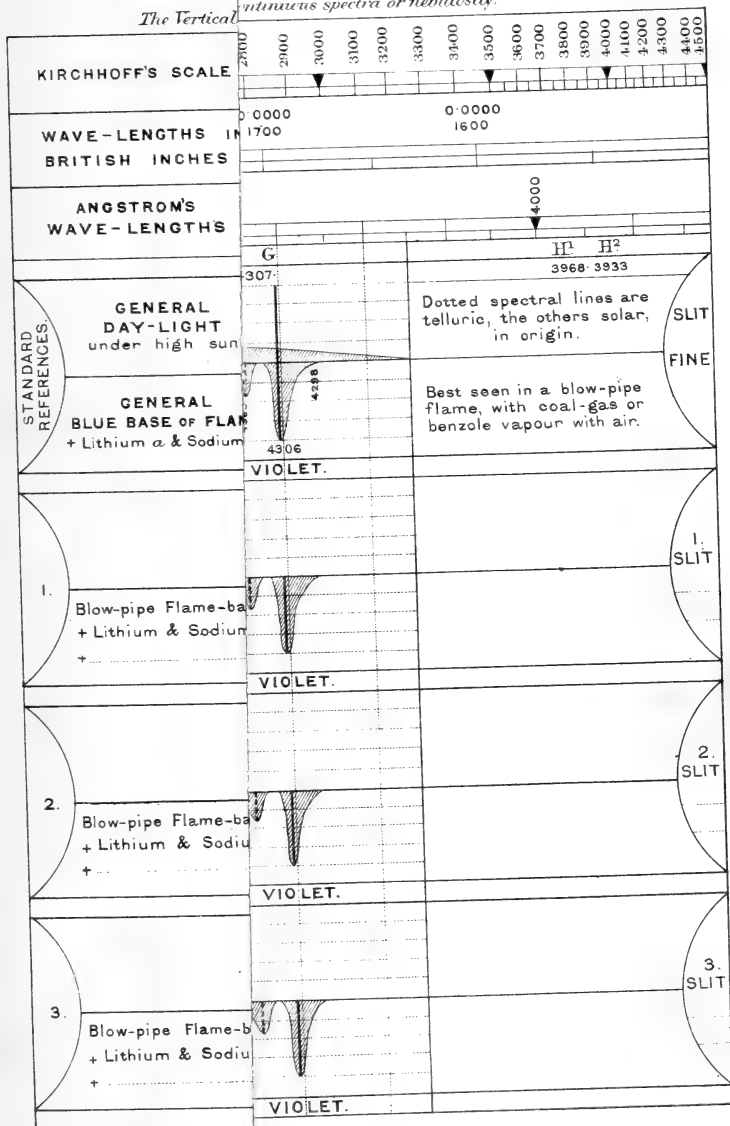
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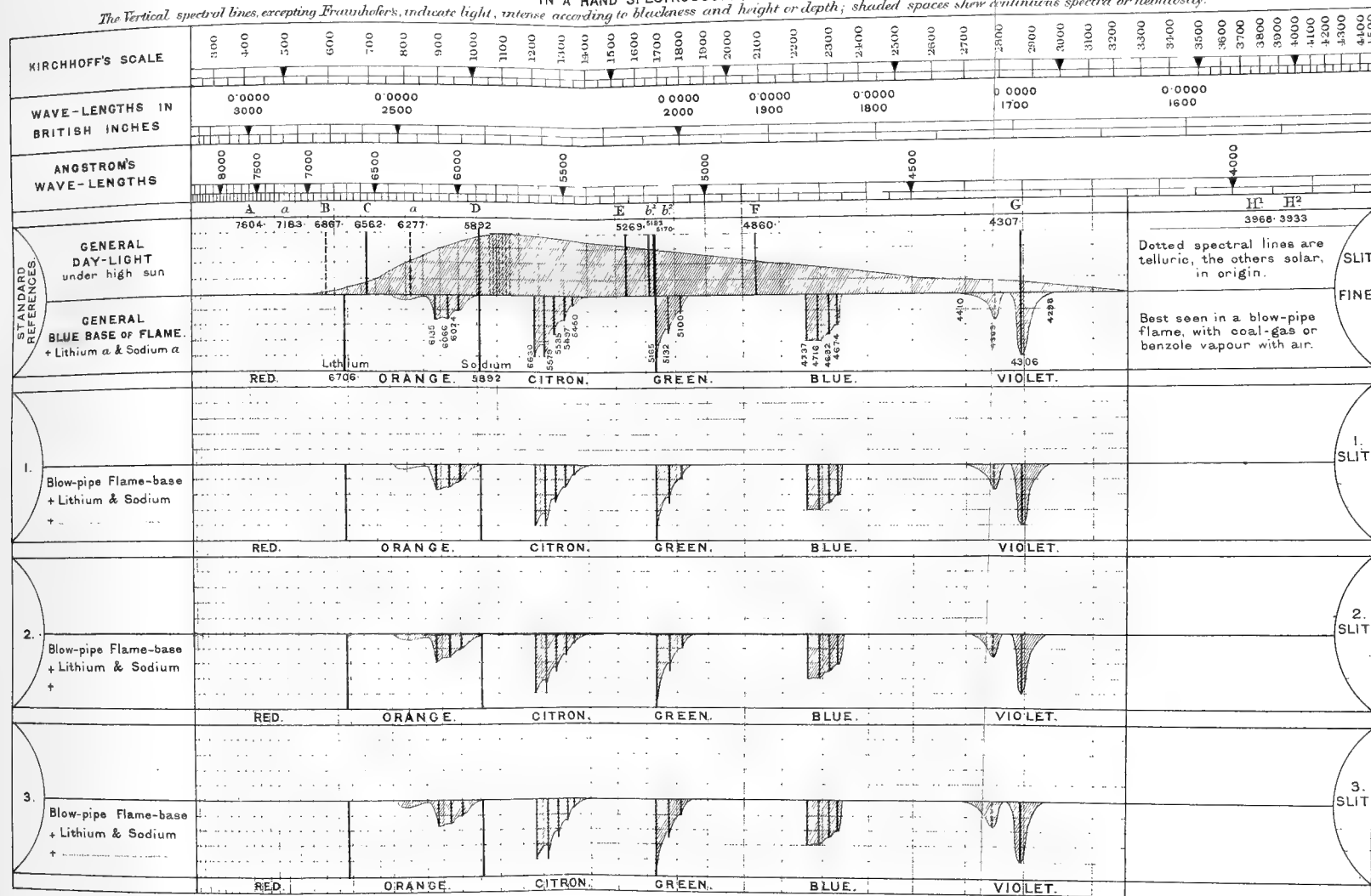
The Vertical continuous spectra or nebulosity.

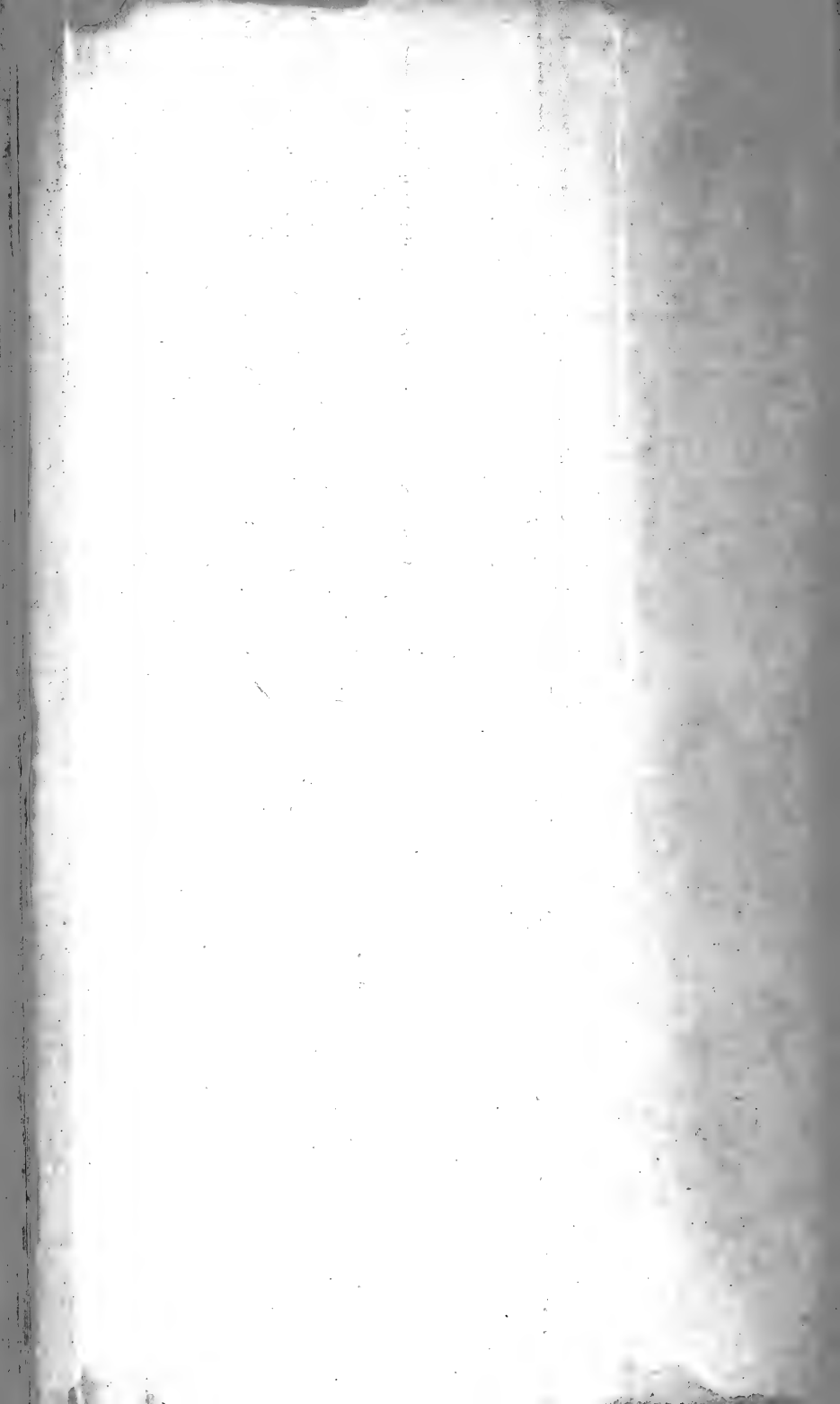




# TABULAR FORM PREPARED FOR SIMULTANEOUS PAIRS OF SPECTRA, UNDER SMALL DISPERSION. IN A HAND SPECTROSCOPE, ONLY.

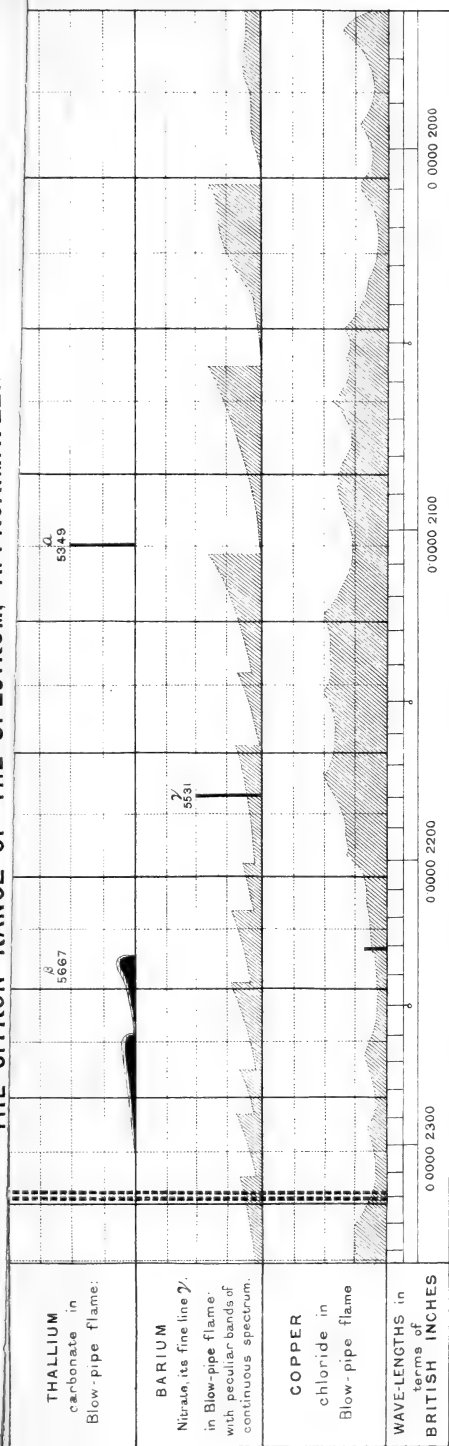
The Vertical spectral lines, excepting Fraunhofer's, indicate light, intense according to blackness and height or depth; shaded spaces show continuous spectra or nebulae.







# THE CITRON RANGE OF THE SPECTRUM, APPROXIMATELY.

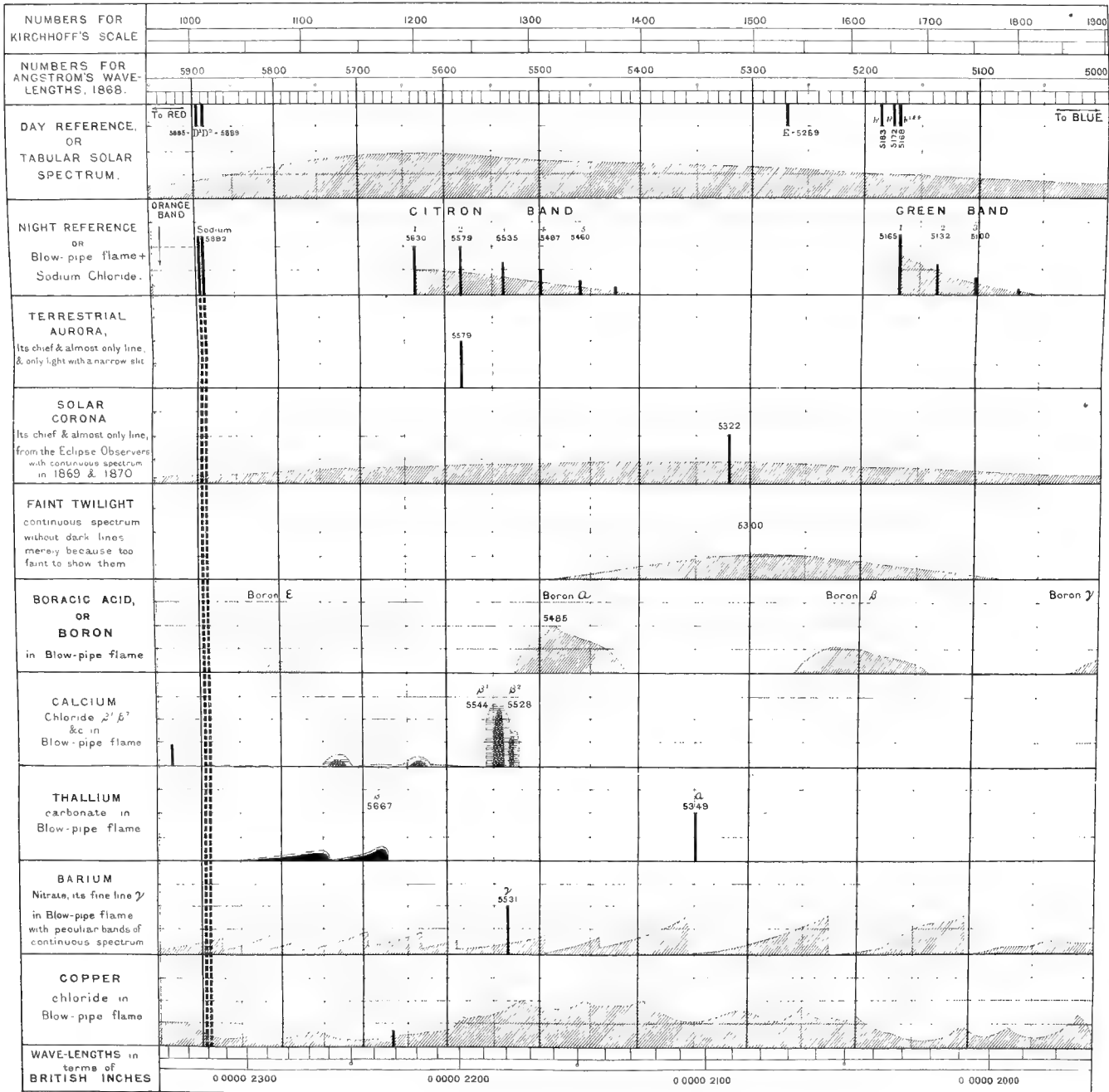




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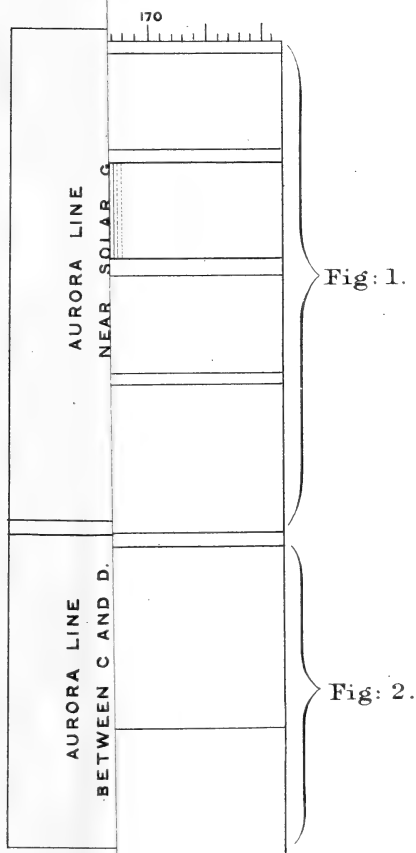
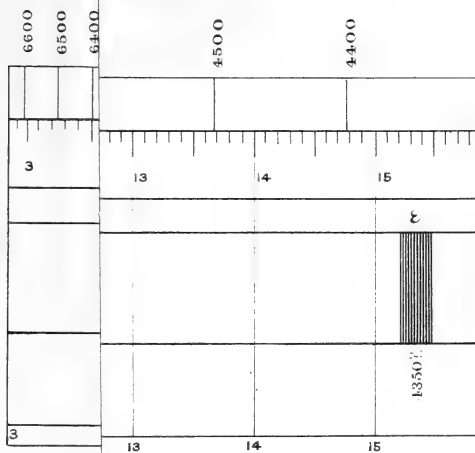
REPRESENTED FROM EYE SKETCHES ONLY.

*Ascending lines, in each horizontal partition, indicate light, intense according to height, descending lines indicate blackness, shaded lines, continuous spectra.*





LINES.





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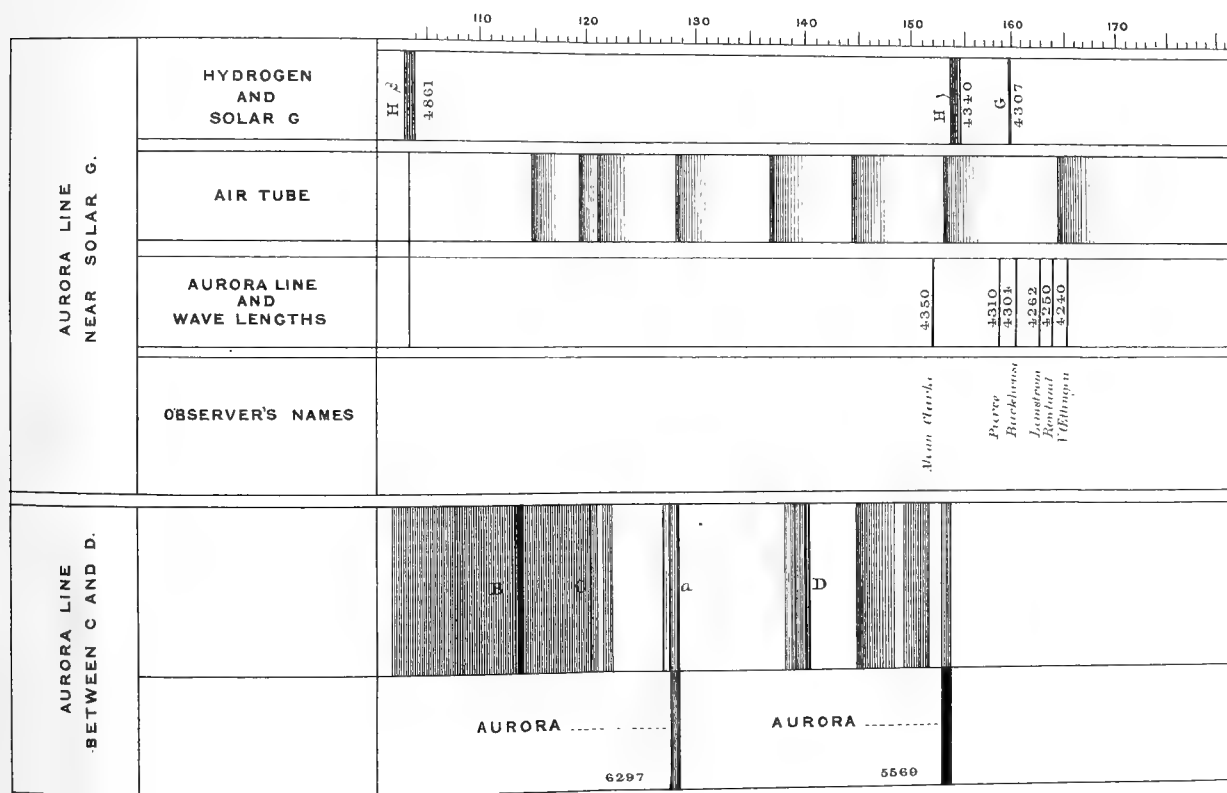
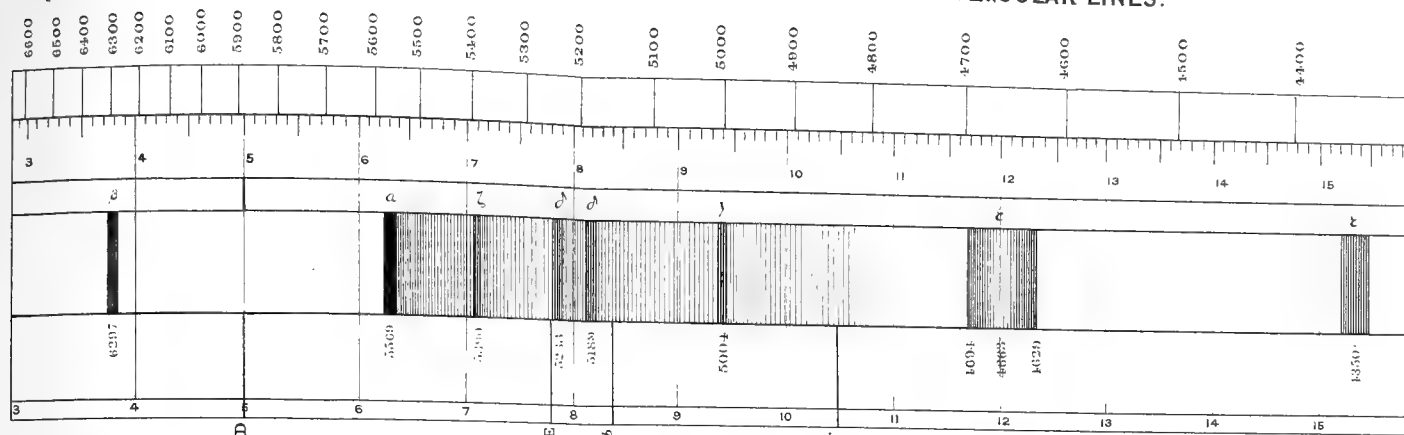
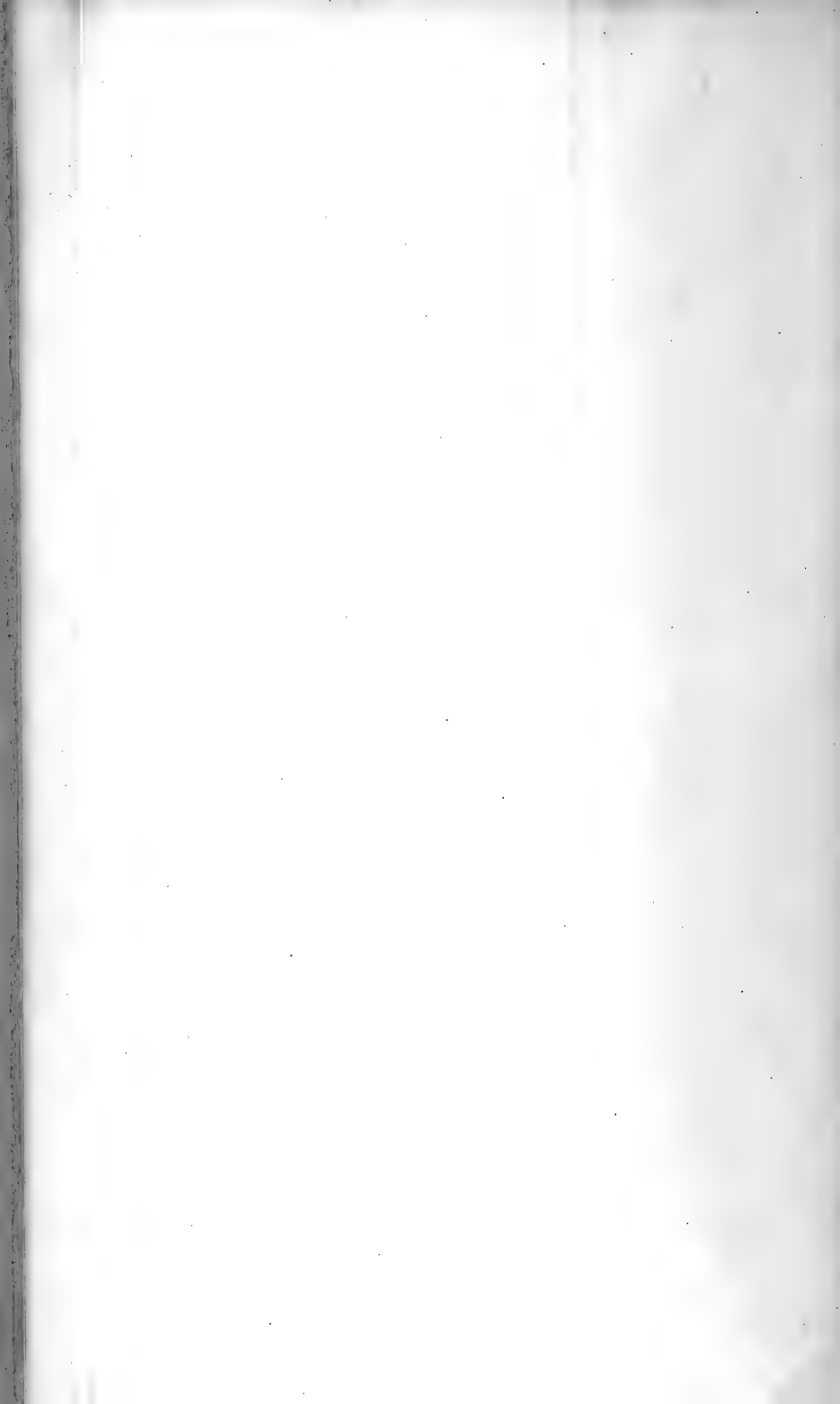
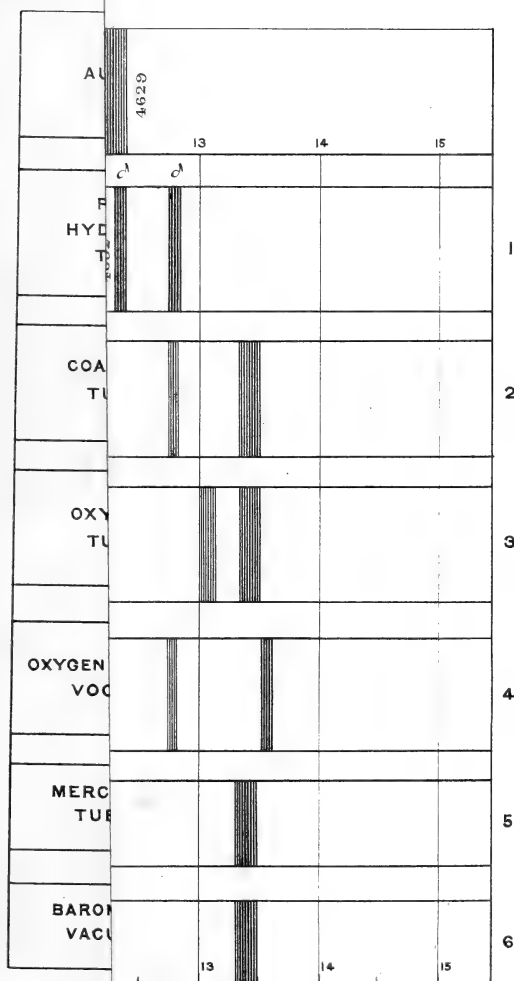


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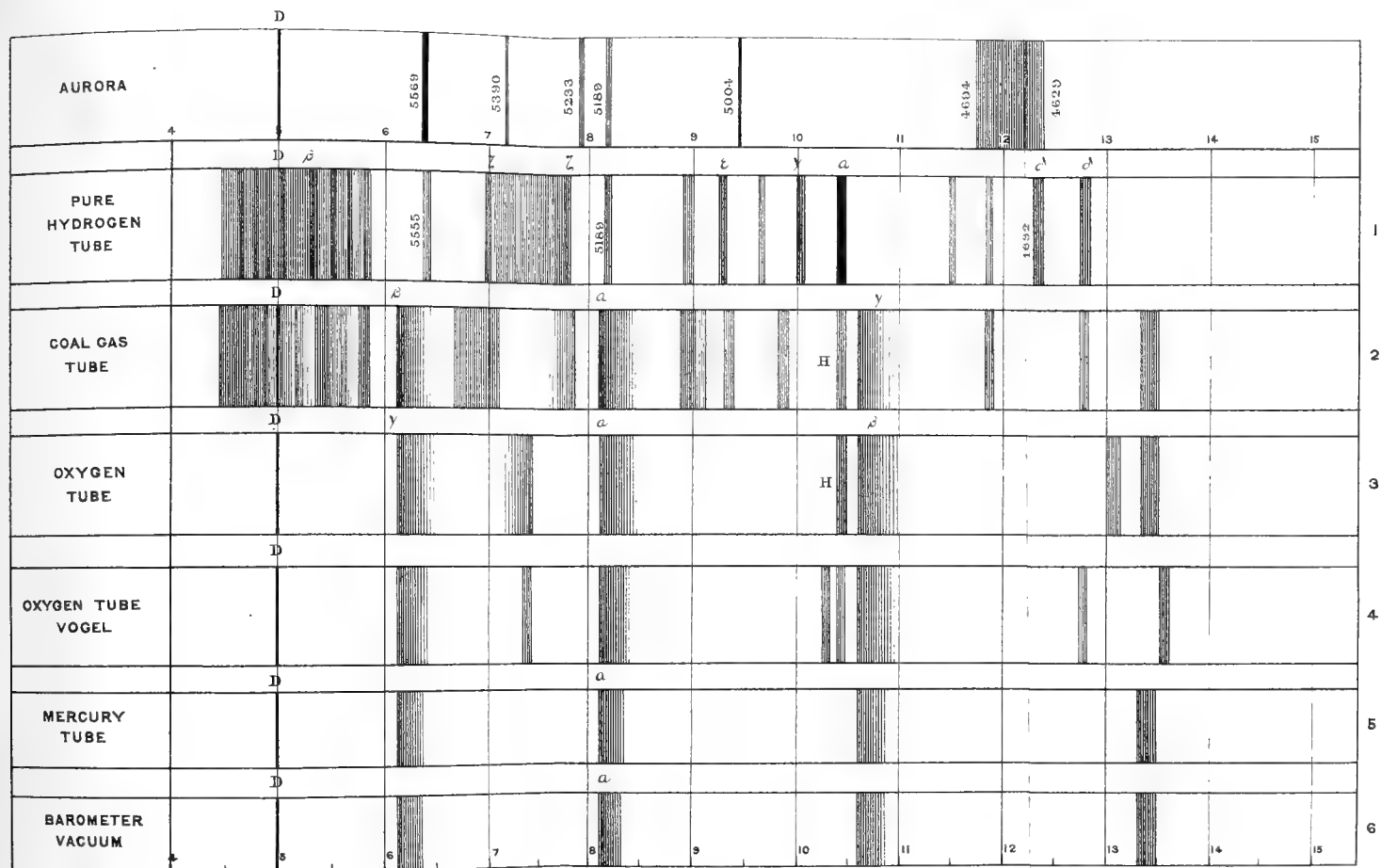


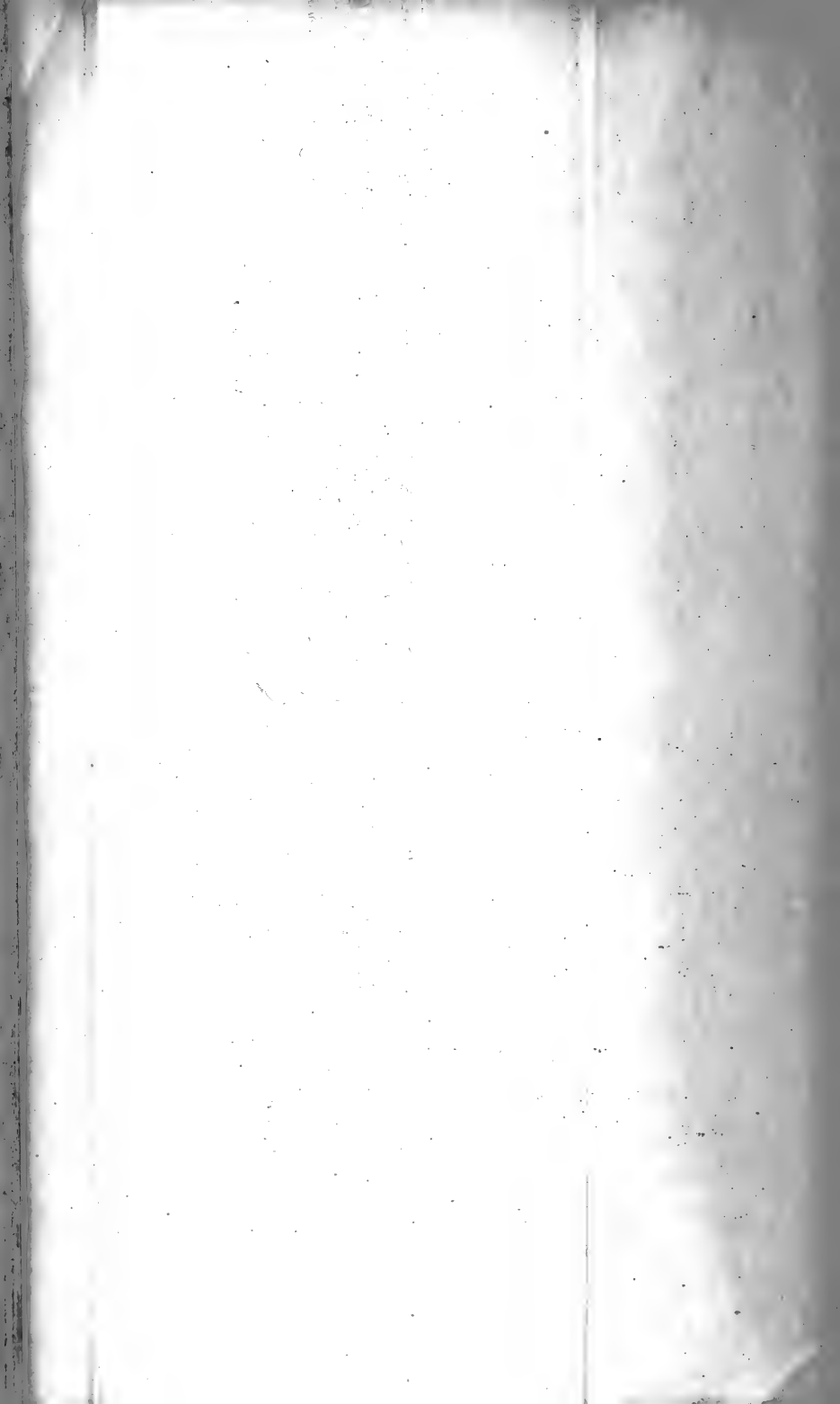


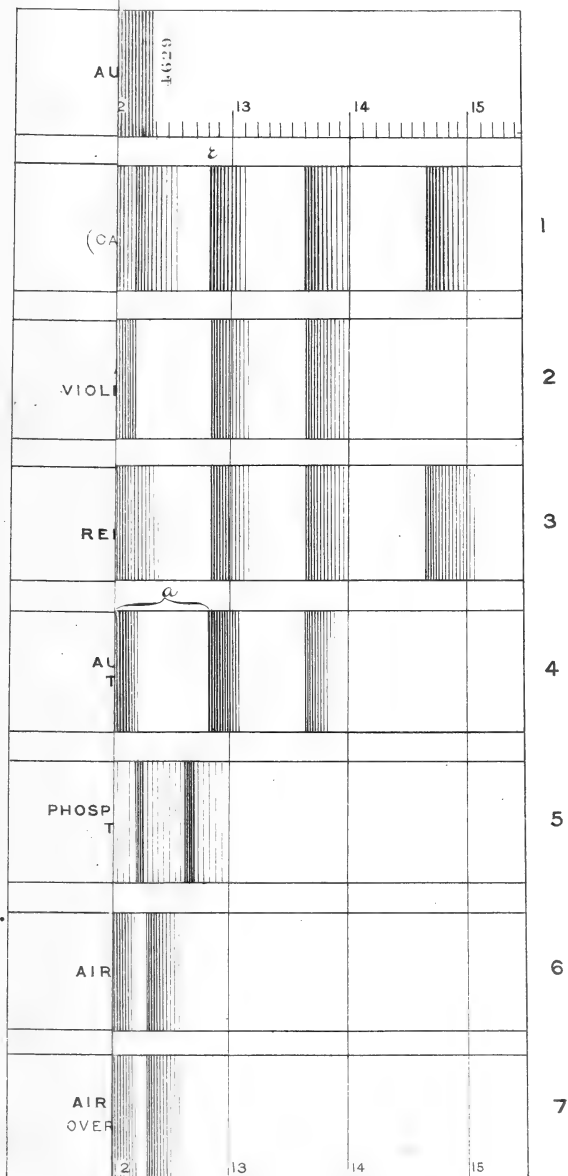




AURORA, HYDROCARBONS, OXYGEN.

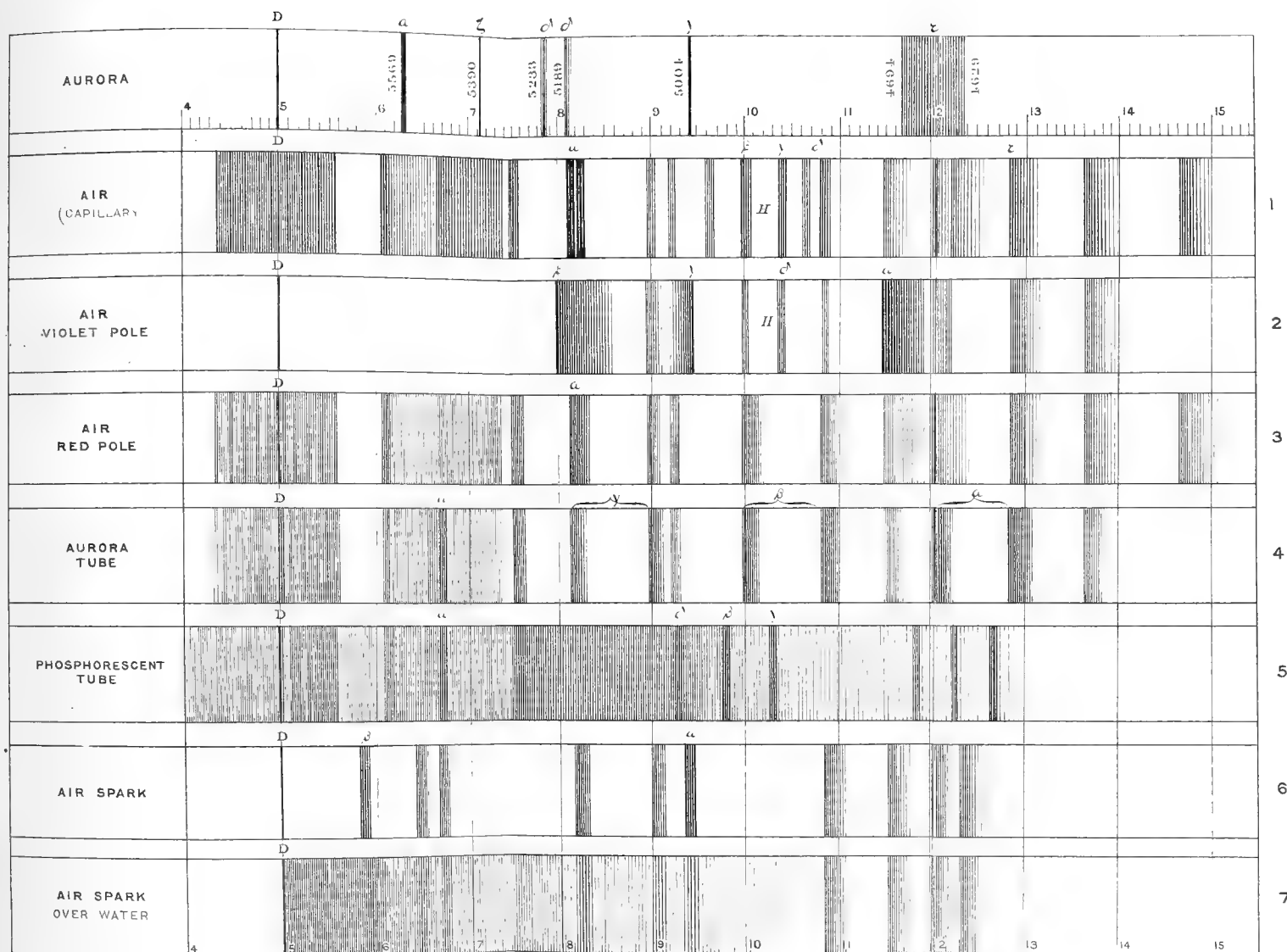


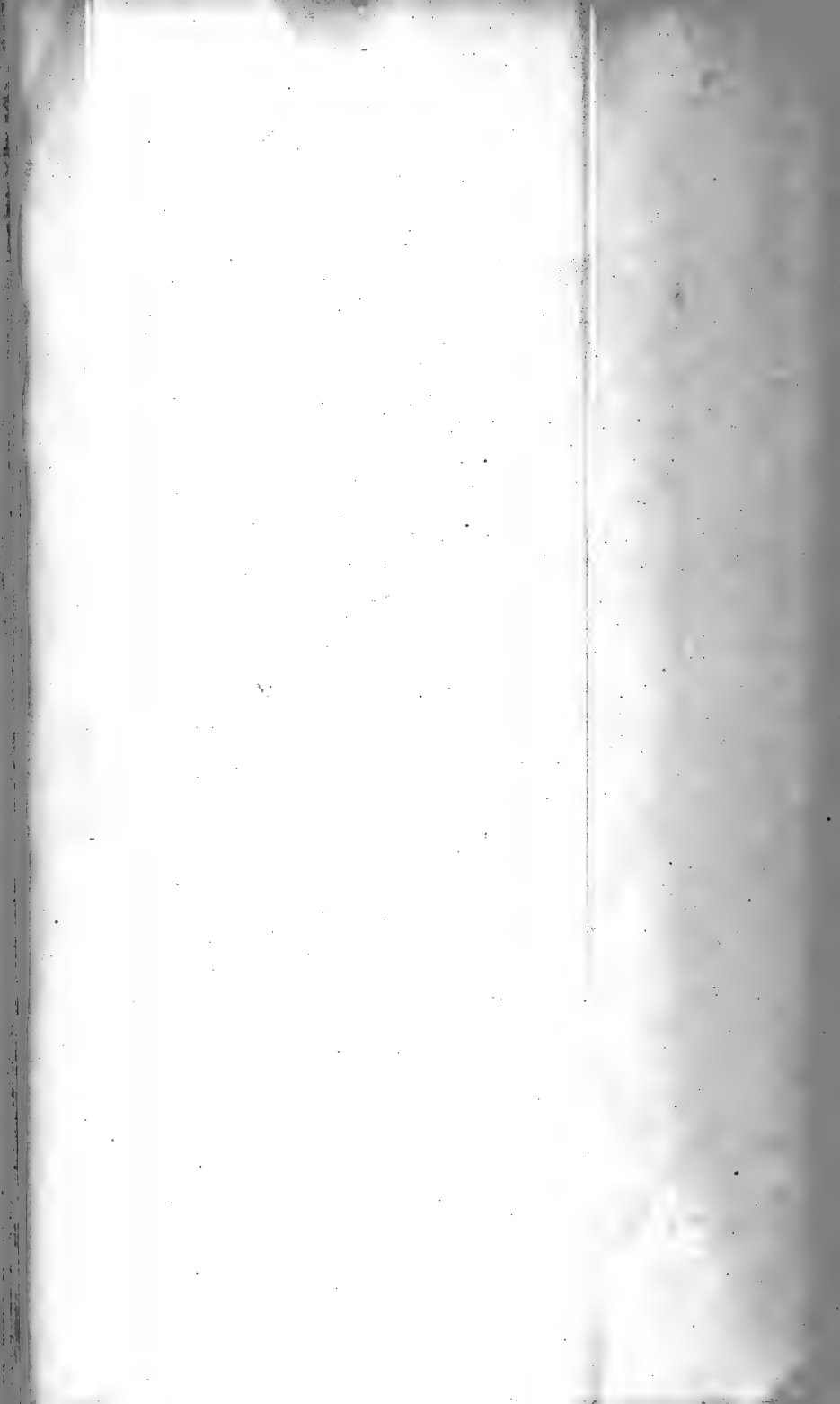






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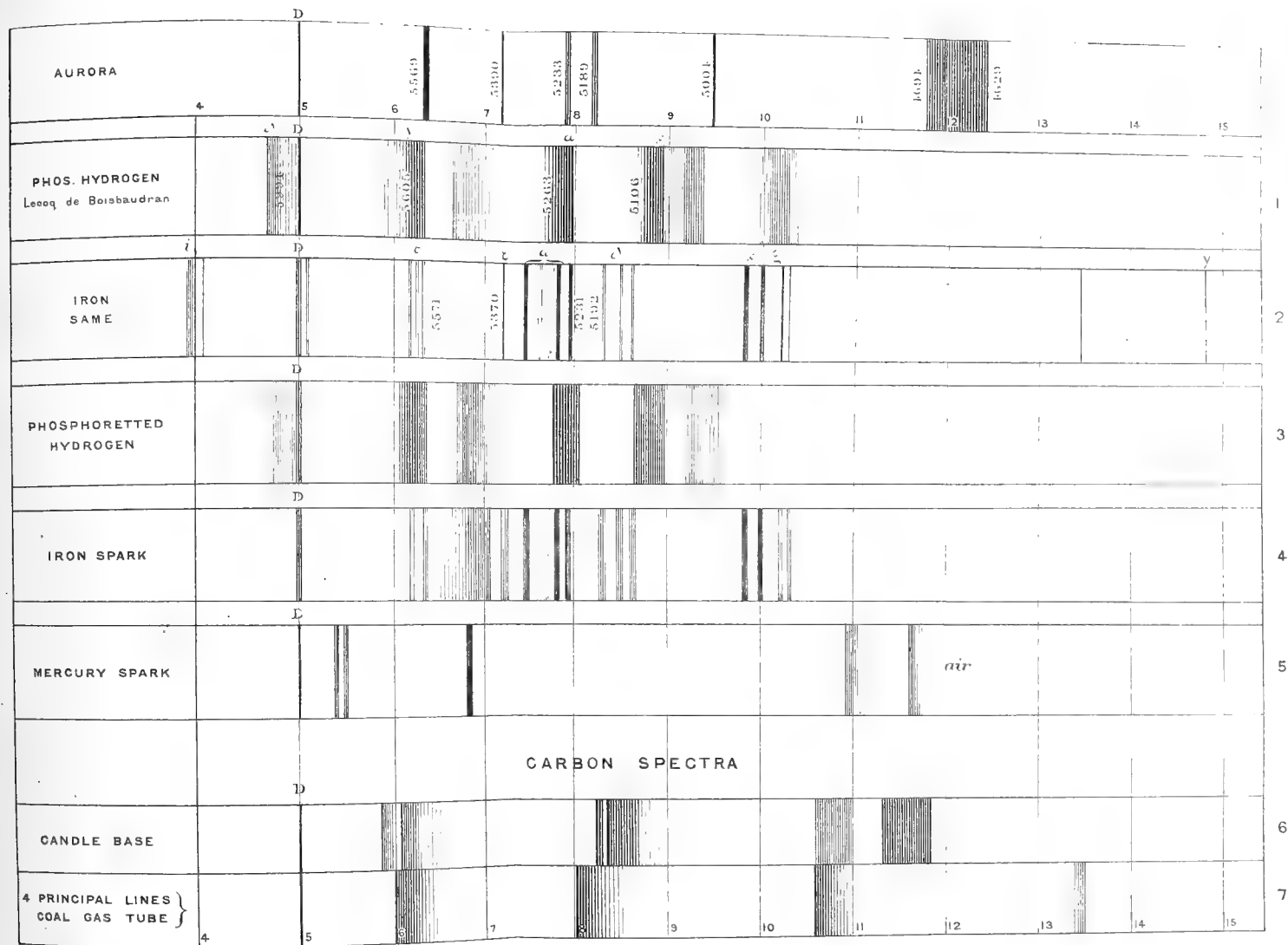
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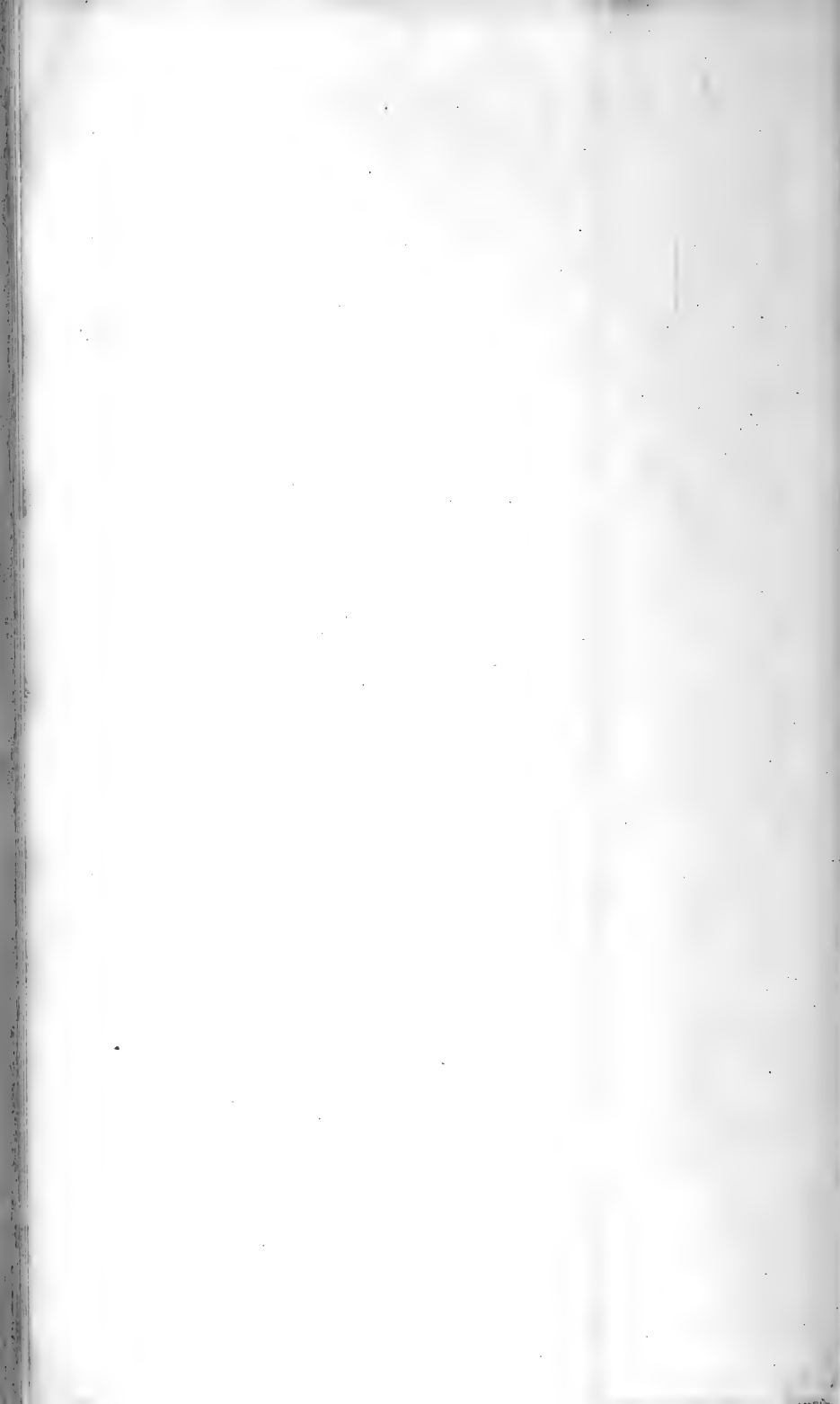
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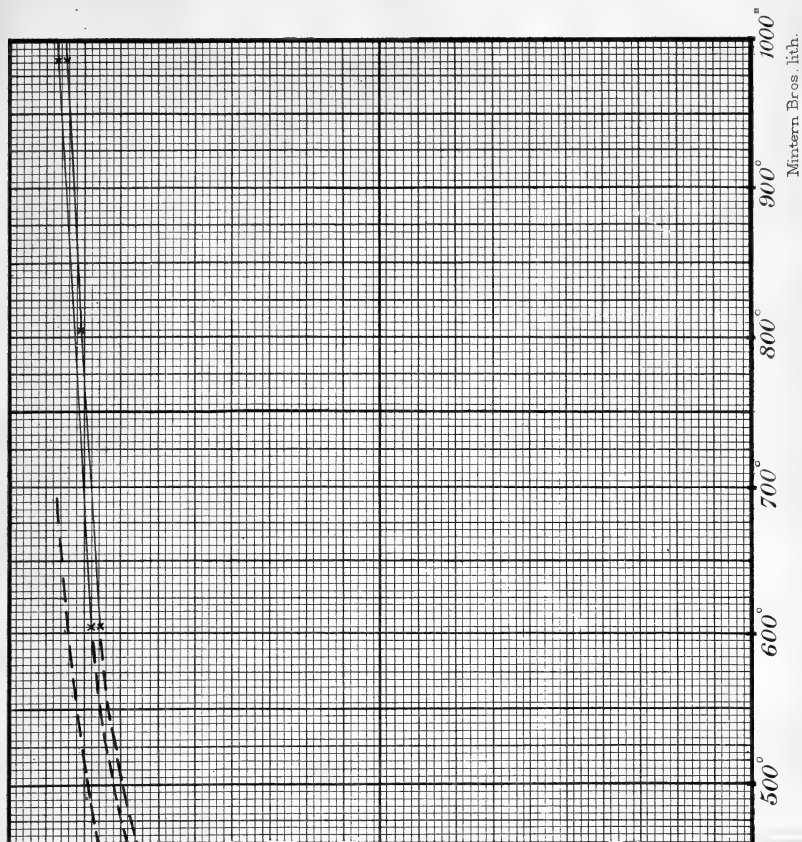
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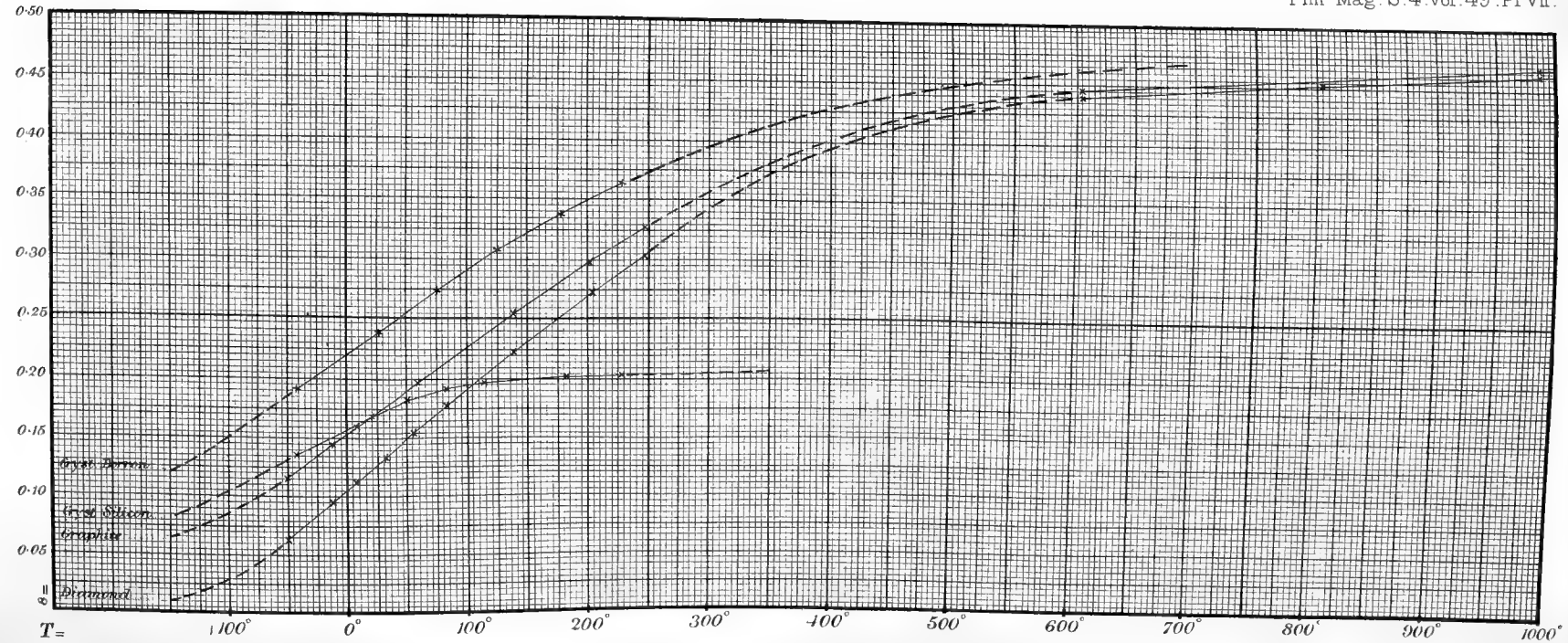
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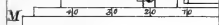




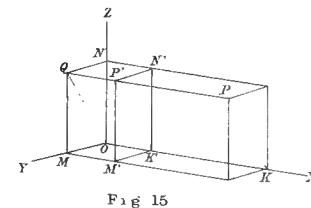
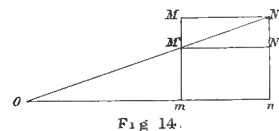
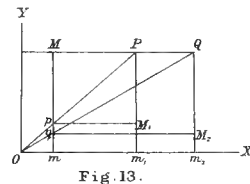
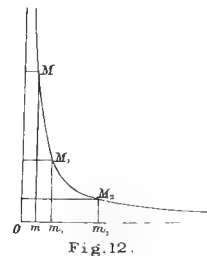
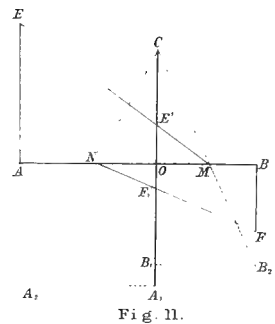
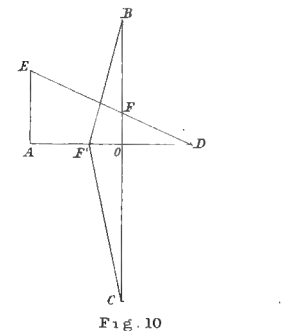
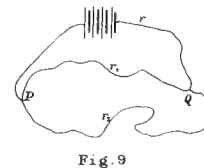
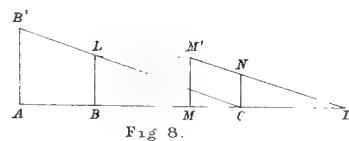
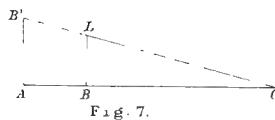
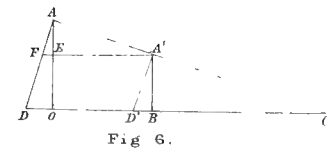
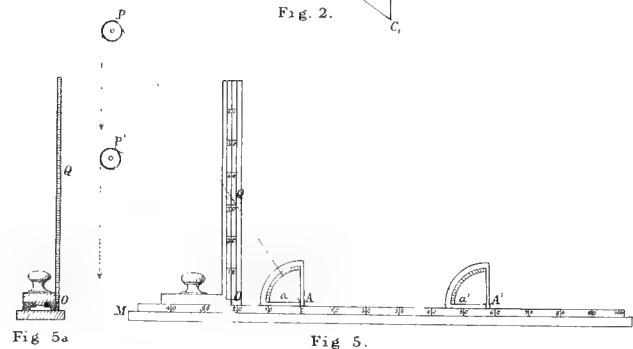
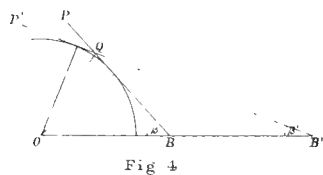
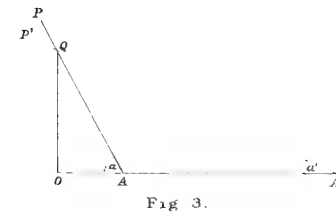
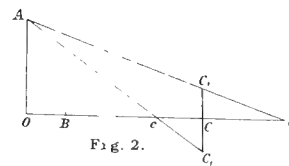
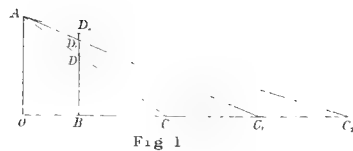


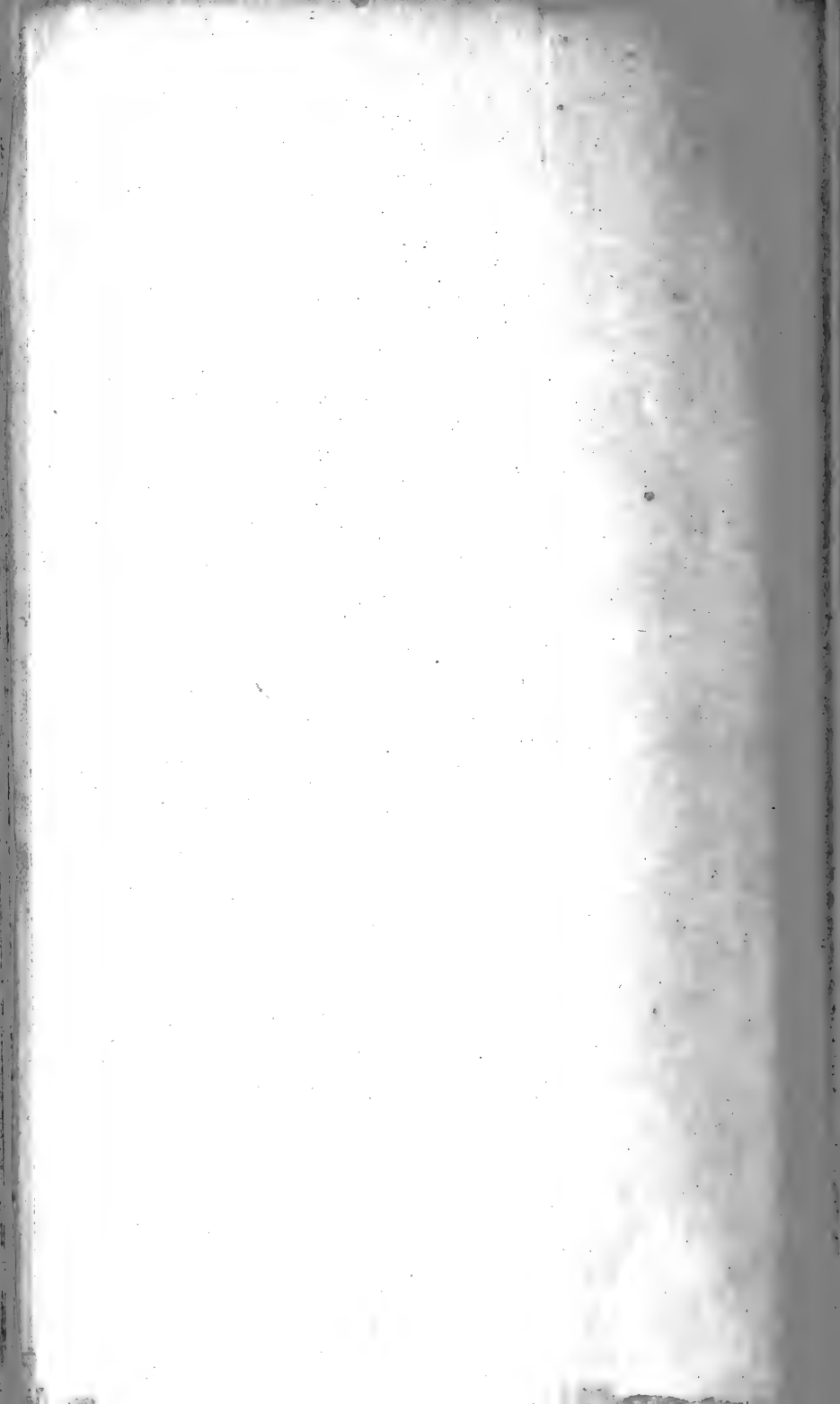












*Lines of Flow and Equipotential lines for two equal opposite poles in an untwisted plane [ $\alpha = 30^\circ$ ;  $\mu = \frac{5}{3}$ ]*

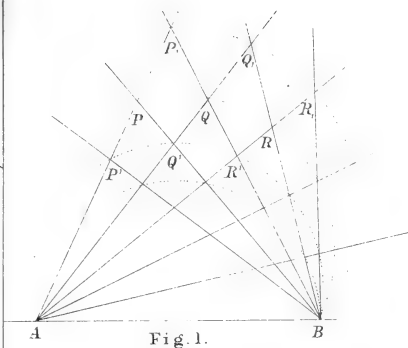


Fig. 1.

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- $BC = h$
- $OD = l$
- $OD' = l'$
- $CP = \ell$
- $AP = r$
- $BP = r'$

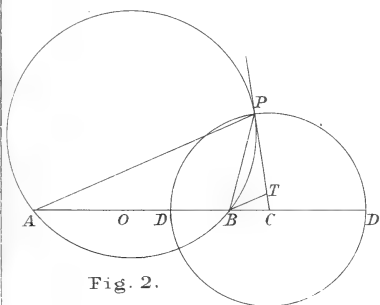


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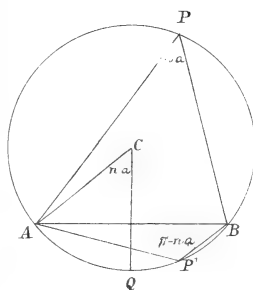


Fig. 3.

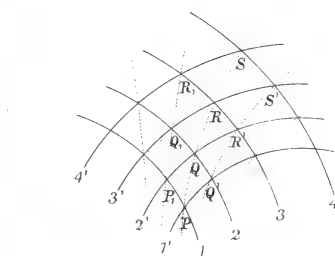
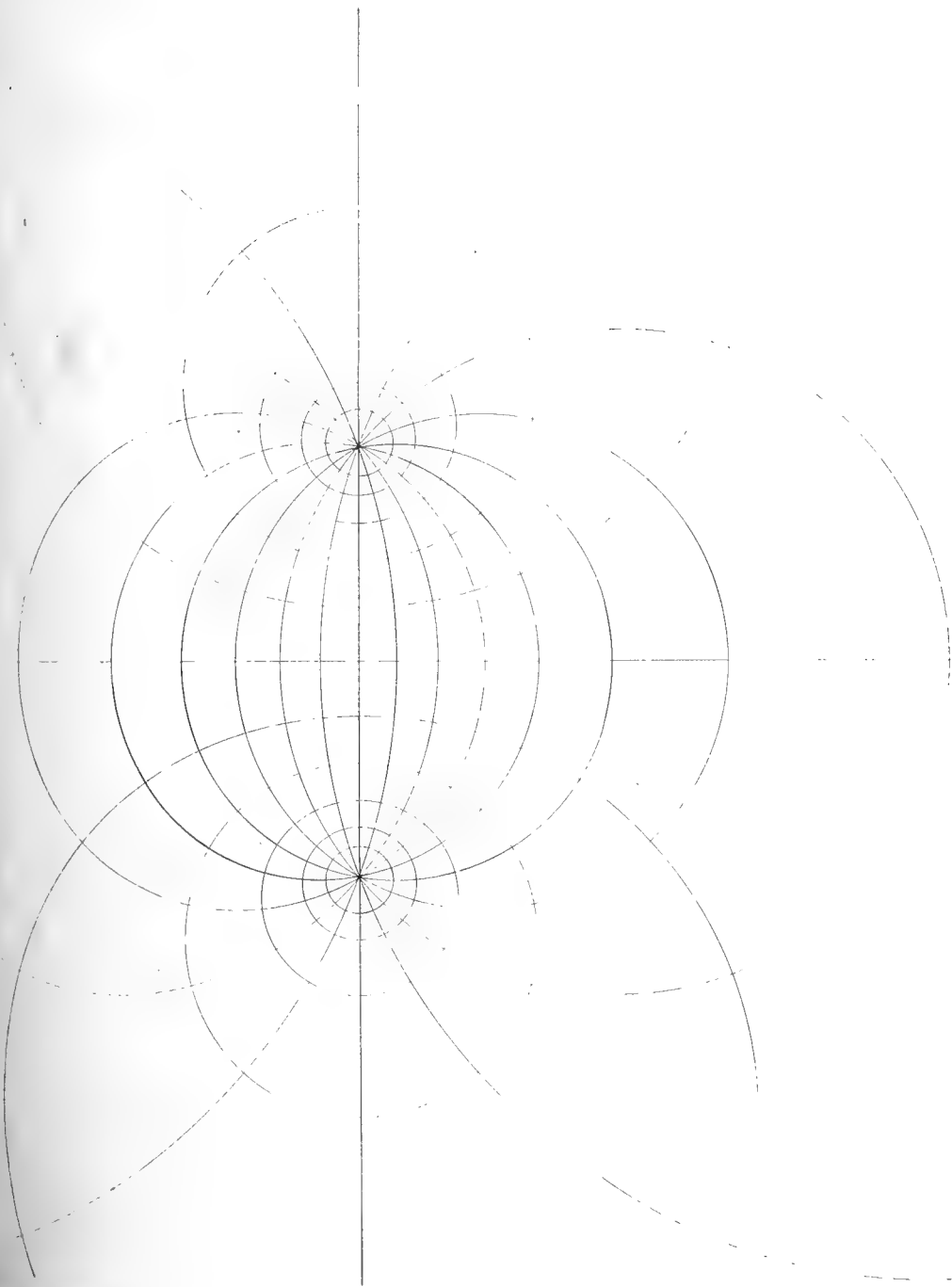


Fig. 4





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Fig. 1

$$\begin{aligned} & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \end{aligned}$$

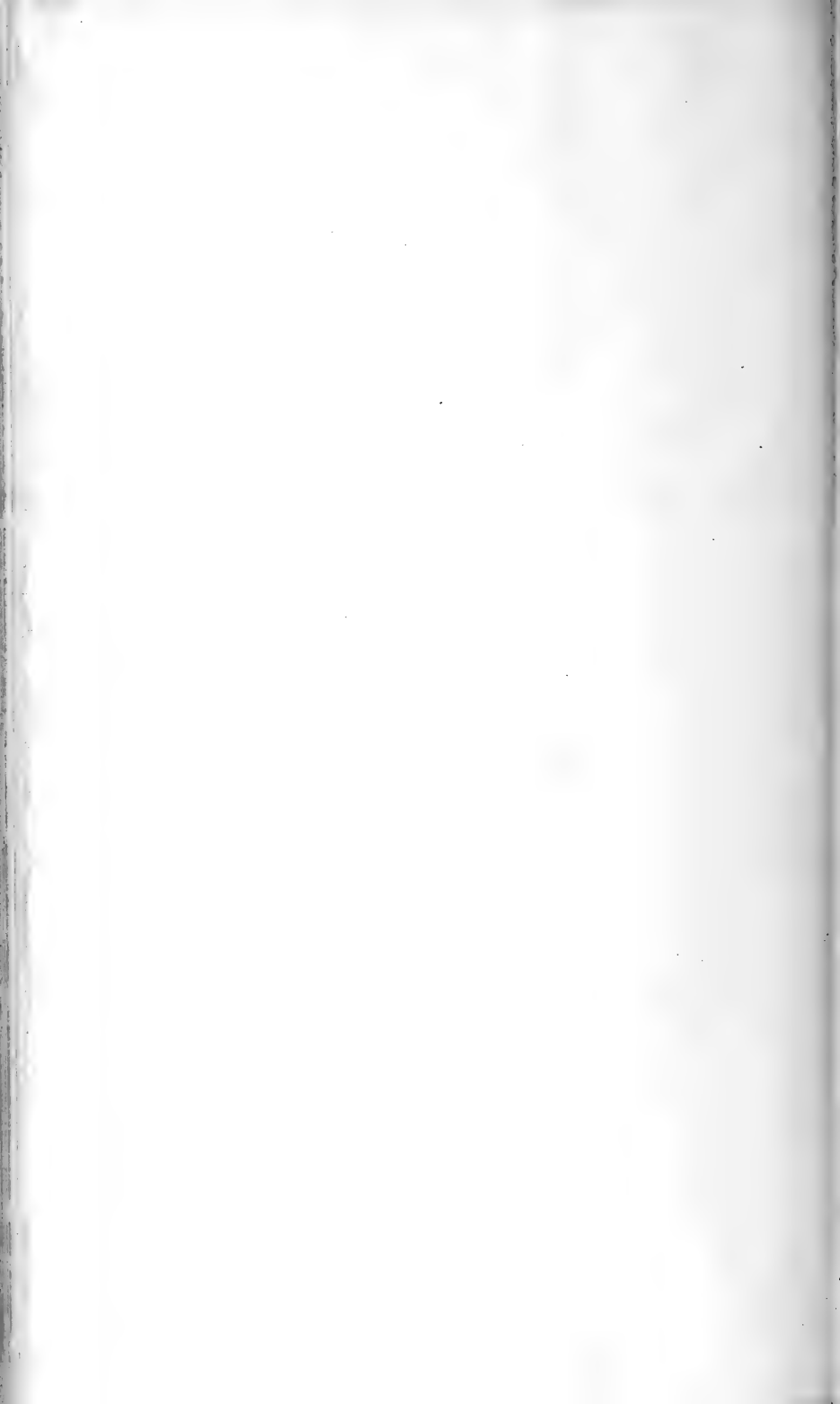
Fig. 2

$$\begin{aligned} & \vec{P} \\ & \vec{Q} \\ & \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \end{aligned}$$

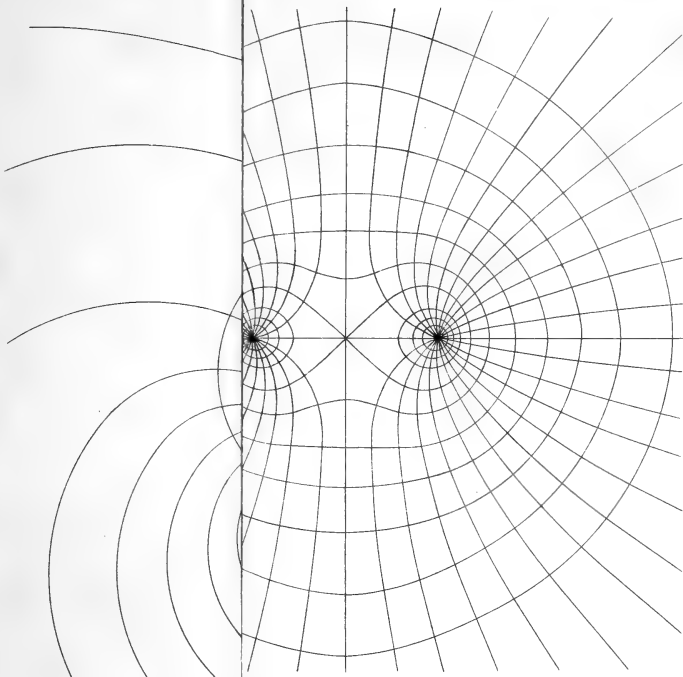
Fig. 3

$$\begin{aligned} & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \\ & \vec{P} \quad \vec{Q} \quad \vec{R} \end{aligned}$$

Fig. 4







Lines for two equal Similar Poles. [ $\alpha = 15^\circ$ ;  $\mu = \frac{3}{2}$ ]

Fig: 3.

Equipotential Line  
Two opposite

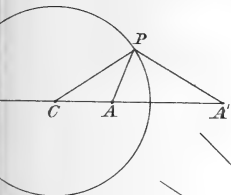
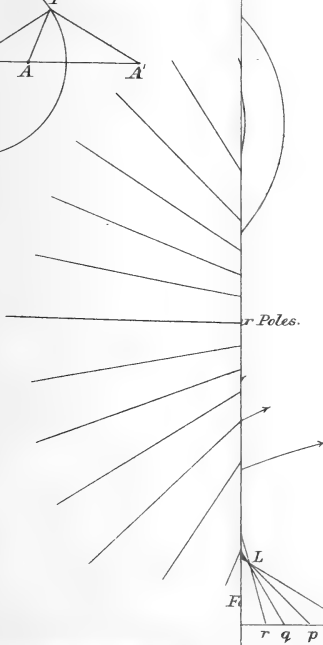
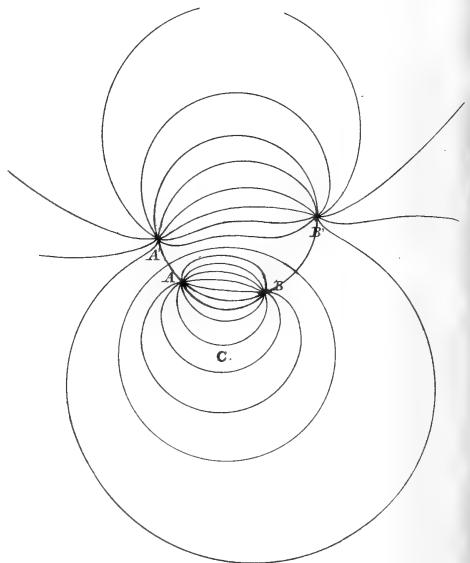


Fig: 5.



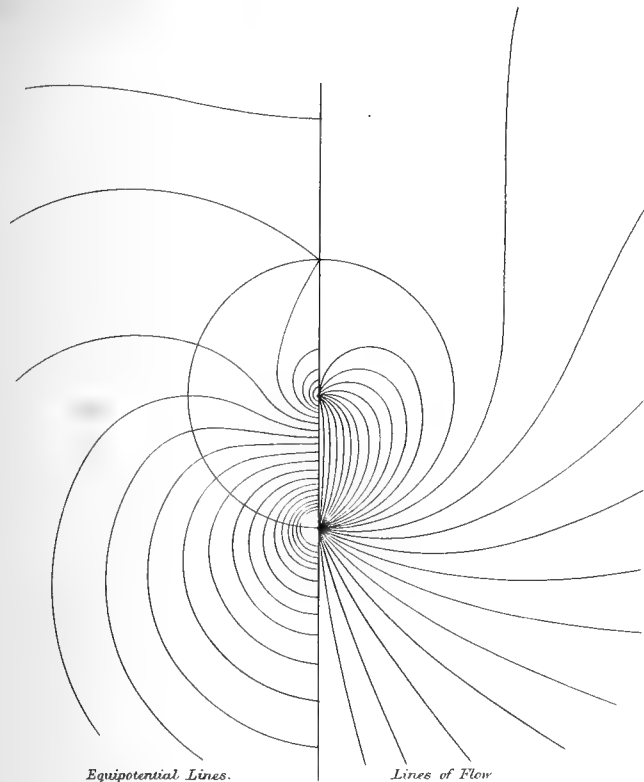
Two Poles.



Four equal Poles: A and A' positive; B and B' negative.

Fig: 9.





Equipotential Lines.

Lines of Flow

Two opposite poles, one twice as strong as the other.

Fig: 6.

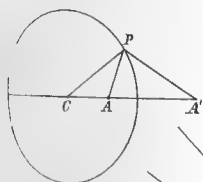


Fig: 5.

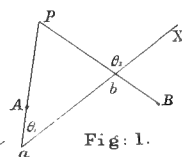
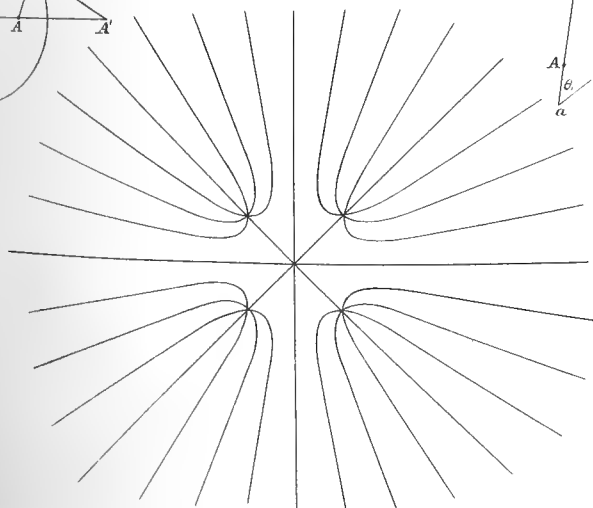
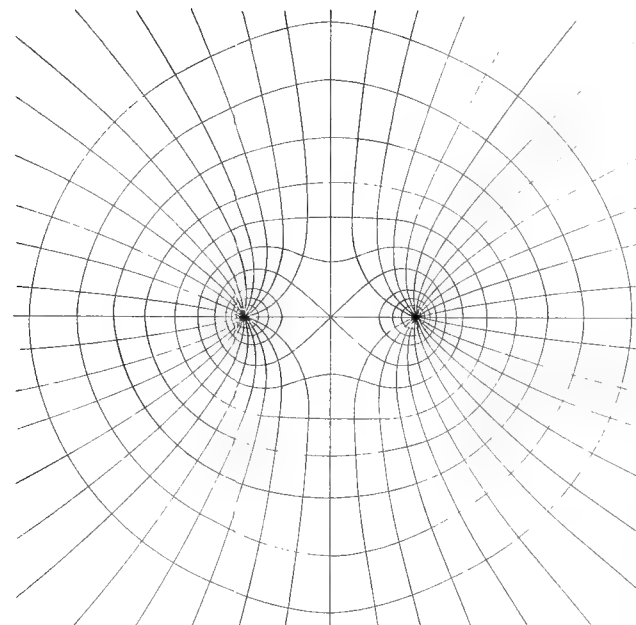


Fig: 1.



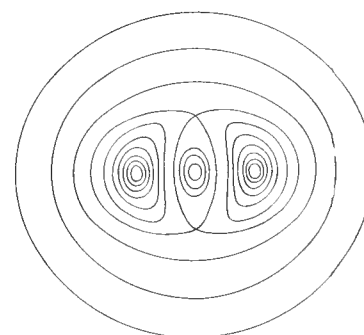
Four Equal Similar Poles.

Fig: 7.



Lines of Flow and Equipotential Lines for two equal Similar Poles. [ $\alpha = 15^\circ$ ,  $\mu = \frac{1}{2}$ ]

Fig: 3.



Loci of Equal Flow for two equal Similar Poles.

Fig: 4.

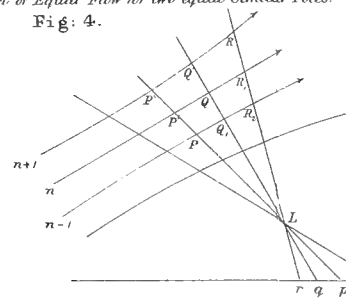
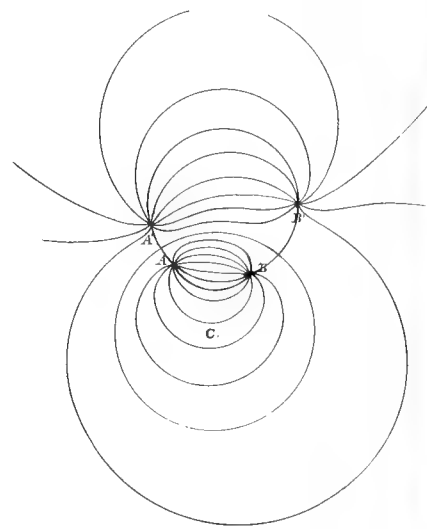


Fig: 2.



Four equal Poles A and A' positive, B and B' negative

Fig: 9.



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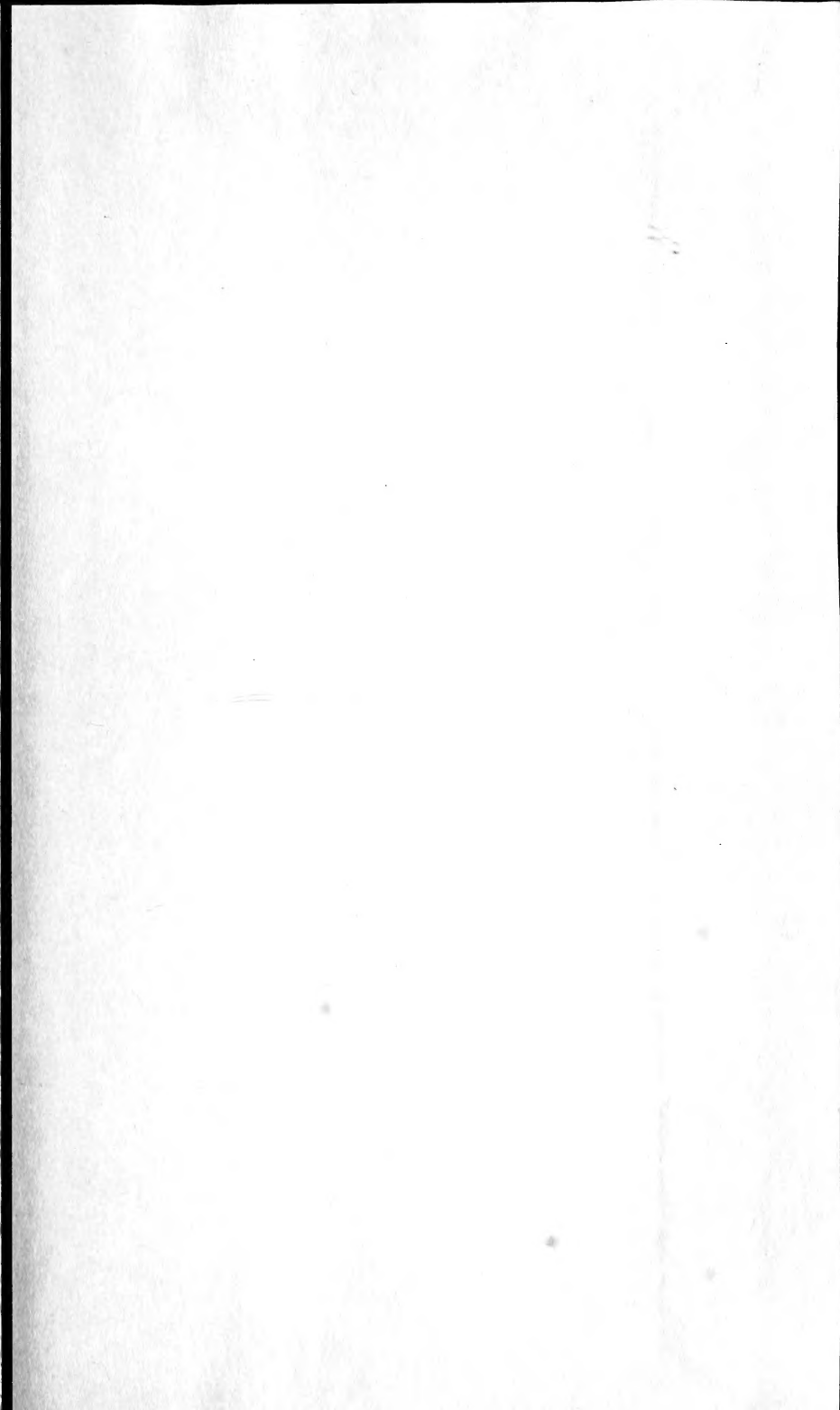
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